Department of Mechanical Engineering

Studies of Syngas Cleaning Technologies Suitable for Power Generation from Biomass Oil Palm Shells

Bridgid Chin Lai Fui

This thesis is presented as part of the requirements for the Award of the Degree of Master of Philosophy of the Curtin University

February 2011

Declaration

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgment has been made.

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

Signature: 

Date: 30th December 2010

To my beloved Family

Abstract

The efficiency of the gas cleaning step is one of the fundamental steps to the successful operation of biomass gasification technologies for power generation. Catalytic cracking is selected as the hot gas cleaning technology for this research using zeolite HZSM-5 catalyst in order to reduce tar produced from palm shells gasification in the laboratory scale fixed bed gasifier. The catalyst load of 2, 5 and 10 weight % of the weight of palms shells has been tested in experiment. Gas chromatographic analysis of the tar produced has been conducted along with the study of biomass gasification index (BGI), emissions of CO, NO, and SO_2. It is observed that the tar contains a high concentration of carbolic acid (5 to 8 volume %) in the gas in the range of oxygen to nitrogen flowrate ratio from 0.10 to 0.15 studied. The carbolic acid concentration decreases in the tar with the oxygen to nitrogen ratio increase. The overall heterocyclic aromatics in the tar content are comparable when operating with oxygen to nitrogen ratio of 0.12 and 0.15.The lowest concentration of carbolic acid has been achieved when 5 weight % of HZSM-5 catalyst is used with a reduction of 99% and 79% for oxygen to nitrogen ratio of 0.10 or 0.15 respectively when compared to the carbolic acid concentration without the presence of the catalyst. At the same time higher percentage of the catalyst results in less chemical compounds found in tar. Tar content increased as lower concentration of oxygen content in gas mixture or larger palm shells particle size was used. Lower CO emission produced when lower oxygen content in gas mixture was used. Oxygen to nitrogen ratio has the most significant effects on the NO production compared to palm shells particle size. Both oxygen to nitrogen ratios and palm shells particle size does not have any significant effects on the SO_2 production. Higher BGI could be obtained if larger palm shells particle sizes are used in this system. Suitable correlations for the tar removal cleanup for syngas derived from biomass oil palm shells at different operating parameters when using HZSM-5 catalyst have been developed from the interpolation of the experimental data obtained.

Acknowledgement

Foremost, I would like to express my warm and sincere gratitude to my supervisor Professor Dr Alexander Gorin for the continuous support of my M.Phil study and research, for his patience, motivation, enthusiasm, and immense knowledge. His guidance helped me in all the time of research and writing of this thesis. I could not have imagined having a better mentor for my M.Phil study. I would also like to gratefully thank Assoc. Professor Dr Chua Han Bing and Dr Farouq Twaiq for the inspirations, creative ideas and valuable assistance that they have provided in various ways.

Furthermore, I would also like to thank Shell Malaysia Limited for their financial support under the research grant "Development of Syngas Cleanup Technologies Suitable for Power Generation from Biomass". At the same time, I would like to thank ITS Testing Services (Malaysia) Sdn Bhd for their assistance in providing gas chromatographic analysis on the tar samples.

A special thanks to my father, Mr Polycarp Chin for his continuous support and guidance to explore all avenues when problem is faced and provided me with all the technical help that I needed.

Last, but not least, I thank my parents for giving me life in the first place, for educating me with aspects from both arts and sciences, for unconditional support and encouragement to pursue my interests, even when the interests went beyond boundaries of language, field and geography. And also, thank God for His inspirations and great help in various ways during the research study and thesis writing, as well as the abundant blessings from Him.

Publications

Chin, L. F. B., A. Gorin, and H. B. Chua. *Biodiversity and Biotechnology Symposium, November 19 - 21, 2008: Tar formation, reduction, and elimination from biomass gasification: recent trends and development.* Kuching, Malaysia: Sarawak Biodiversity Centre.

Chin, L. F. B., A. Gorin, and H. B. Chua. *CUTSE 1st International Conference, November 24 - 27, 2008: Gas cleaning technologies in biomass gasification for power generation.* Miri, Malaysia: Curtin University of Technology, Sarawak campus.

Chin, L. F. B., A. Gorin, F. Twaiq, and H. B. Chua. *CUTSE 2nd International Conference*, *November 24 – 25, 2009: Influence of air-nitrogen composition on the gasification of palm shells biomass.* Miri, Malaysia: Curtin University of Technology, Sarawak campus.

Chin, L. F. B., A. Gorin, F. Twaiq, and H. B. Chua. *International Conference on Environmental Science and Technology, April 23 – 24, 2010: Effect of HZSM-5 zeolite on tar reduction for biomass palm shell gasification in fixed bed reactor.* Bangkok, Thailand: International Association of Computer Science and Information Technology (IACSIT).

Chin, L. F. B., A. Gorin, and H. B. Chua. *ASEAN Australian Engineering Congress, July 25 – 27, 2011: Syngas cleaning technologies suitable for power generation from biomass palm shells.* Kuching, Malaysia: Engineers Australia Malaysia Chapter and Swinburne University of Technology Sarawak campus.

Nomenclature

Notation	***Description***
ANOVA	Analysis of Variance
BGI	Biomass Gasification Index
C_t	Concentration of Tars in Syngas (mg/Nm^3)
CHP	Combined Heat and Power
EFB	Empty Fruit Bunches
ER	Equivalence Ratio
ER%	Percentage Error
ESP	Electrostatic Filters
FC	Fixed Carbon
FCC	Fluid Catalytic Cracking
HHV	High Heating Values
IGCC	Integrated Gasification Combined Cycle
ISTD	Internal Standard
J	Joules
LHV	Low Heating Values
LPG	Liquefied Petroleum Gas
LPM	Litres per Minute
kg	kilogrammes
m	metre
M	Mega
MSW	Municipal Solid Waste
MWe	Megawatts of Electrical Output
N	Normal

PAH	Polyaromatic Hydrocarbons
ppm	Parts per million
RE	Renewable Energy
SCR	Selective Catalytic Reduction
SRC	Short Rotation Coppiced
T1	Dense Bed Temperature (°C)
T2	Freeboard Zone Tempearature (°C)
V_g	Normal Volume of Syngas (Nm^3)
VM	Volatiles Matter
W_i	Initial Weight of Palm Shells before Experiment (g)
W_f	Initial Weight of Palm Shells before Experiment (g)
W_t	Weight of Tars in Syngas (mg)
ZSM-5	Zeolite Socony Mobil-5

Table of Contents

List of Tables

List of Figures

Chapter 1 Introduction

Environmental pollution, diminishing supply of fossil fuels, and uncertainty of world's energy prices are the key factors leading to search for alternative energy resources such as renewable energy (RE). Globally at present, fossil fuels still plays a major part of the world energy consumption although many studies and initiatives have been carried out to find alternative source of RE but it is still not practiced commercially due to its incompetitiveness as compared with fossil fuels. Therefore, continuous development of RE is encouraged and vital to buffer the long-term impact of higher global energy price, and aid to reverse fossil fuel dependency. In the local context under the 9th Malaysian Plan, the Government put efforts to promote RE and energy efficiency as part of the sustainable development agenda as Malaysia progresses towards Vision 2020. From this initiative taken, it clearly shows that Malaysia subscribes to the preservation of the environment and also pursuing the economic development (Wahab, Mokhtar, and Ludin, 2005).

Another advantage of using RE resources is that the supply is never exhaustive since it is constantly replenish through the cycles of nature. RE can be categorised into solar, wind, hydro, geothermal, and biomass energy as an example. Agricultural residues are potentially an attractive feedstock for producing energy as these residues contributes little or no net carbon dioxide to the atmosphere (Ghani et al. 2007) and relatively known as clean feedstock for producing modern energy carriers, such as electricity and transportation fuels in replacement and substitution of fossil fuels. In Malaysia, the agricultural production continued to record positive growth from 2000 to 2005 and expected to expand more in 2010 consistent to the government policy (Chuah et al. 2006). This significantly results in an abundant supply of biomass waste underutilised

which provides the beginning look promising in the view of new emerging biomass energy technologies over other renewable energies.

In general, this is common to consider biomass as the plant material derived from the reaction between carbon dioxide (CO_2) in air, water and sunlight, via photosynthesis, and stored in the biomass as chemical energy. It can be ranged from agricultural crops and agricultural residues; wood and wood residues; to waste streams. Due to its neutral carbon and less sulphur and nitrogen contents, biomass could reduce CO_2 greenhouse effect and sulphur dioxide (SO_2) and nitrogen oxides (NO_x) atmospheric pollution (McKendry 2002a). The chemical composition of biomass varies among species, but basically consists of high but variable moisture, a fibrous structure consisting of lignin, carbohydrates, or sugar and ash (Turn 1999). The main properties of interest when considering the type of biomass to be used as energy source are moisture content, calorific value, proportions of fixed carbon and volatiles ash/residue content, alkali metal content and cellulose/lignin ratio.

In this research, biomass palm shell is selected as the raw feedstock. This is due to the growing global demand for edible oil which has resulted in oil palm to become today world's largest source of edible oil with 38.5 million or 25% of the world edible oil and fat production (MPOC 2008). It is reported that Malaysia and Indonesia are the world largest producer of palm oil with 15.88 million tonnes and 15.9 million tonnes respectively in 2006 (U. S. Department of Agriculture 2007). As the result, palm oil wastes from palm oil production have increased tremendously over the years. It is reported that 1.9 million tonnes of palm shells are generated as solid wastes, at an increase of 5% annually (Yang et al. 2004). Due to huge amount of biomass palm shells generated yearly, countries such as Malaysia and Indonesia have the potential to utilise the biomass effectively to other value products.

Biomass can be converted into three main types of product namely electrical/thermal energy, transport fuel, and chemical feedstock. Conversion of biomass to energy is

undertaken into two main process technologies which are thermo-chemical and bio-chemical/biological. Thermo-chemical conversion is represented either by combustion, gasification, or pyrolysis meanwhile bio-chemical/biological consists of fermentation, anaerobic digestion, or mechanical extraction.

Gasification is considered as one of the most promising thermochemical technologies, which converts solid fuels to synthesis gas (syngas) using gasification agents such as oxygen, air, steam, or combinations of these oxidising agents for wide application such as power generation through gas turbines, production of liquid fuels using Fischer Tropsch synthesis, and production of hydrogen, ethanol and methanol. The few advantages of implementing this technology are no strict constraint to the size and the type of the biomass to be used, the produced gas are applicable for heat/power generation, production of syngas, methane, and hydrogen, and less pollution problems associated with the downstream applications compared with pyrolysis or combustion; and also competitive cost compared to combustion or even to all other electricity supply candidates (*Biomass Technology Group* 2010).

However, there are also some drawbacks of using gasification process. The syngas from all gasification reactors contained particulates, and organic contaminants (tars) which, if not removed, would damage the engine/gas turbine or incur an unacceptable level of maintenance. The efficiency of a gas cleaning technology step is therefore fundamental to the successful operation of power plants.

Although gasification is an old technology with respect to coal based feedstock, it is a developing technology with respect to biomass since only a few types of biomass such as woody and straw feedstock had been successfully applied in this technology and no palm shells feedstock had been used in this process commercially. The most recent research that is performed by previous researchers in Curtin University, Sarawak Campus is generating syngas from biomass palm shells in compartmented fluidised bed gasifer (CFBG) with air as gasification agent focusing only on the main product

content, H_2 and CO (Chok et al. 2009). However, no studies were carried out to investigate the effect of the byproducts especially tar produced from syngas under different operating parameters using biomass palm shells suitable for gas turbine application.

Gas turbines are highly encouraged to be chosen over gas engine for power generation as it is capable of producing large amounts of useful power for a relatively small size and weight, mechanical life is long and the corresponding maintenance cost is relatively low as motion of all its major components involve pure rotation instead of reciprocating motion as in a piston engine, and wide variety of fuels can be utilised (Langston and Opdyke 1997).

To select gas cleaning technologies for biomass gasification, catalytic cracking is chosen as the hot gas clean up in the laboratory scale gasification process in this research as it is considered to be one of the most promising methods for tar elimination and does not generate wastewater (Saxena et al. 2008, 1916). In the current investigation, HZSM-5 catalyst is selected as the catalyst for tar cracking in the fixed bed reactor since this catalyst belongs to zeolite group which have the potential to eliminate tars from fuel gas (Abu et al. 2004, 6915). The advantages of using this catalyst compared with amorphous catalysts are related to their acidity, better thermal/hydrothermal stability, better resistance to nitrogen and sulphur compounds, tendency toward low coke formation, and easy regenerability (Sherzer and Gruia 1996). Other than that, zeolites are commercially available, cheap, and zeolite has gained experience using this catalyst in FCC units, which offers better practical insight (Buchireddy et al. 2010). Nonetheless, the main disadvantage is the coke formation which results in rapid deactivation of these catalysts (Abu et al. 2004, 6915). And also, very limited research has been performed to evaluate zeolites for tar removal applications (Buchireddy et al. 2010). Since no studies had been carried out using this catalyst on gasification processes using palm shells feedstock, therefore, it will be worthwhile to study the catalytic cracking effect of this catalyst on the tar produced

from biomass palm shells gasification.

Hence, the key objective of this research are to carry out analysis to select an appropriate gas cleanup technology suitable for biomass derived syngas, specifically in the removal of tar for gas turbine application since one of the major challenges is the tar formation in biomass gasification which results in condensation and clogging in the downstream process.

This thesis is organised into five chapters as outlined below.

- ***Chapter 1*** defines the scope, overall aim and the structure of this thesis.
- ***Chapter 2*** represents analysis of the various syngas cleanup technologies in practice and proposes the cleanup technologies suitable for biomass oil palm shells for power generation gas turbine.
- ***Chapter 3*** discusses the experimental pinch scale process for a proposed gas cleanup technologies system.
- ***Chapter 4*** presents the experimental investigation of the cleaning efficiency of tar removal with respect to the variation in operating parameters such as air to nitrogen ratio, temperature, presence of catalysts, the particle sizes of biomass oil palm shells and percentage of HZSM-5 catalyst used and suitable equations developed from the experimental results on the prediction of tar content.
- ***Chapter 5*** draws conclusion from this study and outlines the recommendations for future research.

Chapter 2 Analysis of Technologies and Biomass Feedstock

2.1 BIOMASS GASIFICATION

2.1.1 Historical Milestones of Biomass Gasification

Gasification is considered as one of the oldest technologies with respect to coal based feedstock and was originally developed in the 1800s for the purpose to produce "town gas" for lighting and cooking. The development of this technology had been divided into 5 main stages and had undergone a significant transformation in the past 50 years (with the most rapid changes in the last two decades) which is further demonstrated in Table 2-1 (Hutchison 2009).

It is seen that gasification of coal had been well-developed and established over the years but biomass gasification is merely a developing technologies which had never fully been embraced on a larger commercial scale. The renewed interests in biomass gasification are due to the sharp increase in the price of the crude oil and are evident from the number of commercial as well as developmental projects that are shaping up globally (Babu 2006). According to studies conducted by Shell International Petroleum Company and Intergovernmental Panel on Climate (DOE 2006), biomass could satisfy between one-quarter and one-half of the world's demand for energy by the middle of the 21st century. For example, it is anticipated through statistical analysis that the usable biomass per year in Japan might amount to 26 million kiloliter crude oils of heat equivalence (Murukami 2007, 244). Leung et al. (2004) reported that electricity produced from biomass is relatively far much cheaper compared to electricity from fossil fuels. As evidenced from previous researchers, biomass gasification could provide an attractive alternative to the well-established thermal treatment systems for the recovery of energy from solid wastes.

Table 2-1: The milestones of gasification technology development since 1850s (modified from Hutchison 2009).

Year	***Transformation of Gasification Technology***
1850-1940	- Gasification was first used to produce "town gas" for light and heat. And until development of natural gas supplies and transmission lines in the 1940s and 1950s – virtually all gas for fuel and light was produced from the gasification of coal.
1940-1975	- The second stage of gasification began during World War II when German engineers used gasification to produce synthetic fuel. This technology was exported to South Africa in the 1950s, where it was further developed to produce liquid fuels and chemicals.
1975-1990	- The next stage in the evolution of gasification began after the Arab Oil Embargo of 1973. In reaction to that event and the ensuing "energy crisis," the U.S. government provided financial support for several proof-of-concept gasification projects, including the world's first Integrated Gasification Combined Cycle (IGCC) electric power plant. Another seminal event during this period was conversion of Eastman Chemical's flagship manufacturing plant petroleum to syngas from coal.
1990-2000	-The fourth stage of gasification's development began in the early 1990s when government agencies in the United States and Europe provided financial support to four medium-sized (≈250 MWe) projects to further "demonstrate" the feasibility of the IGCC process.
2000-present	- The current stage in the evolution of gasification began when commercial developers started building IGCC power plants without government subsidies. These new IGCC facilities (all outside the United States) are adjacent to refineries when petroleum coke and other residual hydrocarbons are readily available.

2.1.2 Current Status of Gasification Technology

The development of biomass gasification technology has been benefited from the well-establishment of coal gasification (Maniatis 2001). However, both of these technologies are not directly comparable due to differences between feedstock, char reactivity, proximate composition, ash composition, moisture content, and density (Bridgwater, Toft, and Brammer 2002).

Bridgwater and Evans (1993) summarises all known recent and current activities on biomass gasification around the world that are either at a demonstration or commercial scale or have been developed to a point where they can be considered into large scale commercial applications as shown in Table 2-2. The table also enlists the gasification technologies which can be potentially considered to be implemented to generate over 5 MWe. The selections of gasifier type most preferred by the listed organisation are bubbling fluid bed, circulating fluid bed and fixed bed whereby most of their future plan is to aim in generating electricity.

Lastly, the gasification technologies developed for power generation and discussed in Bridgwater and Evans (1993) are presented in Table 2-3. It is observed that Aeriampianti organisation had successfully generated electricity in 6.7 MW_e whereas Bioflow and Pacific International Center for Higher Research Technology (PICHTR) still under commissioning stage. Meanwhile the rest of the other organisations are still under design, evaluation and deferred stage.

Table 2-2: Recent and current gasification processes

(modified from Bridgwater and Evans 1993).

Gasifier Type	*Organisation*	*Country*	*Current Status*	*Future Plans*
Bubbling Fluidised Bed				
Atmospheric	**JWP Energy Products (EPI)**	USA	Steam for power	Not known
	Southern Electric International	USA	Process heat	Not known
	University of Sherbrooke	Canada	Development	Electricity
	Vrije Universiteit Brussel (VUB)	Belgium	Design	Not known
Pressurised	**IGT**	USA	Demonstration	Electricity; methanol later
	HTW	Germany, Finland	Co-firing for electricity, ammonia	Electricity, syngas
	Tampella Power	Finland	Testing	Electricity
Circulating Fluidised Bed				
Atmospheric	**Ahlström**	Finland	Process heat	None
	Battelle Columbus	USA	Development	Licensing
	Gotaverken	Sweden	Process heat	Not known
	Lurgi GmbH	Germany	Process heat	Process heat, electricity
	TPS (Studsvik)	Sweden	Process heat; electricity	Electricity
Pressurised	**Bioflow (Ahlström/Sydkraft)**	Finland	Demonstration	Electricity
Indirectly heated fluid bed	MTCI	USA	Design	Electricity through steam
Fixed Bed				
Atmospheric	**Bioneer**	Finland	Heat	Not known
	Sofresid	France	Heat	Not known
	Volund	Denmark	Development	Electricity
	Wellman	UK	Process Heat	Electricity
Pressurised	General Electric	USA	Development	Electricity
Entrained Flow				
Pressurised	Veba,	Germany	Development	Not known
	Texaco	USA	Co-firing for power	Electricity
Two Stage Pyrolysis - Gasification				
Atmospheric	**Thermoselect**	Switzerland	Demonstration	Waste disposal

*Processes in **bold** face either have been or are being seriously considered for large scale commercial applications.

Table 2-3: Gasification-to-electricity systems installed, proposed or planned (modified from Bridgwater and Evans 1993).

Organisation	*Gasifier*	*Technology**	*Biomass*	*Generator**	*Status*	*MWe*
Aeriampianti	TPS	CFB	Wood (poplar)	Steam turbine	Operational	6.7
Bioflow	Ahlström	Pressure CFB	Wood chip	Gas turbine CC	Commissioning	6
Elsam	Tampella	Pressure FB	Wood (SRC)	Gas turbine CC	Design	7
ENEL	Lurgi	CFB	Wood (SRC)	2 Gas turbines CC	Design	12
General Electric	GE	Updraft	Eucalyptus wood chips	Not specified	Design	-
Global Environment Facility (GEF)	Not decided	Not decided	-	Gas turbine CC	Evaluation	27
Pacific International Center for High Research Technology (PICHTR)	IGT	Pressure O_2 FB	Bagasse	Not specified	Commissioning	2-3
North Powder	JWP (EPI)	FB	Wood and agricultural waste	Steam turbine	Not known	9
MTCI	MTCI	FB	Black liquor	Gas turbine	Design	4
Vattenfall	Tampella	Pressure FB	Wood chips, forest residue, paper mill waste, willow, straw with coal and alfafa	Gas turbine	Deferred	60
VUB	VUB	Fluid bed	Wood	Gas turbine (Brayton)	Design	0.6
Yorkshire Water	TPS	CFB + Cracker	Willow and poplar short rotation	Gas turbine CC	Design	8

*** FB = Fluid Bed; CFB = Circulating Fluid Bed, CC = Combined-Cycle Operation, SRC = Short Rotation Coppiced**

2.1.3 Gasification Reactions and Principles

A gasification system is made up of three main elements: (1) the gasifier, to produce the combustible gas; (2) the gas cleanup system, necessary to remove harmful compounds from the combustible gas; (3) the energy recovery system (Belgiorno et al. 2003, 3).

Biomass gasification involves two major processes, pyrolysis followed by gasification. Pyrolysis is defined as the thermal degradation either in the complete absence of oxidising agent, or with such a limited supply that gasification does not occur to an appreciable extent. The amount of the three products (gas, liquid and char) produced depends on the pyrolysis method and process condition. The pyrolysis takes place at a lower temperature above 50°C meanwhile gasification takes place at a higher temperature above 1000°C. Air, steam or oxygen or combinations of these are commonly used as oxidant and fluidising media in most gasifiers.

Regardless of gasifier types to be discussed in Section 2.2, the bio-fuels must undergo drying, pyrolysis, oxidation and reduction steps to convert the fuel from a solid phase into a gas phase (Lin 2005, 8).

Gasification process involves two types of reaction, which are exothermic and endothermic reaction. Heat can be supplied either through direct or indirect gasification in order to fulfil the endothermic reaction.

Exothermic Reaction

Combustion:

$$C + O_2 \rightarrow CO_2 \qquad (\Delta H = -394\,MJ/kmol) \tag{2.1}$$

Partial Oxidation:

$$C + \frac{1}{2}O_2 \rightarrow CO \qquad (\Delta H = -111\,MJ/kmol) \tag{2.2}$$

Methanation:

$$C + 2H_2 \rightarrow CH_4 \qquad (\Delta H = -75\,MJ/kmol) \tag{2.3}$$

Water Gas Shift:

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (\Delta H = -41\,MJ/kmol) \tag{2.4}$$

Steam Methane Reforming:

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \qquad (\Delta H = -206\,MJ/kmol) \tag{2.5}$$

Endothermic Reaction

Steam Carbon Reaction:

$$C + H_2O \leftrightarrow CO + H_2 \quad (\Delta H = +131 MJ/kmol) \tag{2.6}$$

Boudouard Reaction:

$$C + CO_2 \rightarrow 2CO \qquad (\Delta H = +172 MJ/kmol) \tag{2.7}$$

Direct gasification occurs when an oxidant gasification agent is used to partially oxidise the feedstock. The oxidation reactions supply the energy to keep the temperature of the process up.

If the process does not occur with an oxidising agent, it is called **indirect** (*allothermal*) gasification whereby an external energy source is required. Indirectly heated gasifier systems carry out both gasification and combustion simultaneously, but in physically separated enclosures that can be imbricate or spaced from each other (Levenspiel 2005, 5074).

Indirectly heated gasifiers have the great advantage of producing high hydrogen content in the product gas, but the disadvantage of high methane and tar concentration due to low operation temperature when compared with the directly heated gasifiers (Zuberbühler, Specht, and Bandi 2005). To upgrade this gas to syngas quality, downstream reforming/cracking units are necessary.

The gasification agent involved in direct gasification is either oxygen or air meanwhile steam is used for indirect gasification. The heating value of the gas produced will vary based on the nitrogen content in the gasification agent shown in Table 2-5. Although air gasification gives the lowest gas heating value due to nitrogen dilution, it is more widely used in industries in avoidance of the requirement for costly oxygen supply, the complexity and cost of multiple reactors in steam or pyrolytic gasification when two reactors are required (Bridgwater 1995, 634). Produced gas from air gasification is

suitable for boiler, engine, and turbine operation, but not for pipeline transportation due to its low energy density, while oxygen gasification is limited for pipeline distribution and for use as synthesis gas conversion for example, to methanol and gasoline. Table 2-4 also shows the exemplary product gas composition for different gasification agents.

Table 2-4: Producer gas heating values and average product gas composition from different gasification agents (modified from Belgiorno et al. 2003 and Zuberbühler, Specht, and Bandi 2005).

Process	***Gasification Agent***	***Producer Gas Heating Value (MJ/Nm^3)***	***Volume (%)***					***H_2:CO***
			H_2	***CO***	***CH_4***	***CO_2***	***N_2***	
Direct Gasification	Air	4-7	15	20	2	15	48	0.75
Pure Oxygen Gasification	Oxygen	10-12	40	40		20		1
Indirect Gasification	Steam	15-20	40	25	8	25	2	1.6

2.1.4 Desirable Syngas Quality for Various Applications

The composition of syngas from biomass gasification varies with the reactor type, feedstock, and processing conditions. Table 2-5 shows the desirable syngas quality for different applications. Each application has its own specifications; therefore, it is not possible to define one set of standard requirement of syngas for all applications. For low technology applications such as cement kiln or co-firing systems, where the product gas is simply burned to provide heat, the raw fuel may be used with little or no cleanup. However, high technology systems such as gas turbine or a system using synthesis gases requires much cleaner fuel gases. Hence, the syngas quality is dependent on the respective technology to be applied to.

Table 2-5: Desirable syngas quality for different applications

(modified from Ciferno and Marano 2002).

Component / *Application*	**H_2/CO**	**CO_2**	**Hydrocarbons**	**N_2**	**H_2O**	**Contaminants Limit (ppm)**
Fuel gas for turbine	Unimportant	Not critical	High	Unimportant	Unimportant	< 0.2 -1 alkali metals
Fuel gas for boiler					Low	< 1.2 alkali metals
Synthetic fuels	0.6	Low	Low	Low	Low	< 1 ppm sulphur, low particulates
Methanol	~ 2.0	Low	Low	Low	Low	
Hydrogen	High	Unimportant	Low	Low	High	

2.2 GASIFIER

Gasifiers are used in different industries such as chemical, petrochemical and utilities. Different types of gasifiers have been designed and developed to fulfil different industries requirement as syngas quality differs from different type of gasifiers. The selection of gasifier is crucial to achieve the desired syngas quality for the end use application.

2.2.1 Classification of Gasifier

There are two types of reactors that are commonly used or practised for gasification of biomass which are fixed bed and fluidised bed reactors. **Fixed bed reactors** are subdivided into updraft and downdraft gasifiers as shown in Figure 2.1. Updraft, also known as counter current mass flow, means that the feedstock and the reactive agent (e.g. air or steam) flow in opposite directions; the opposite concept applies with regard to downdraft (co-current mass flow).

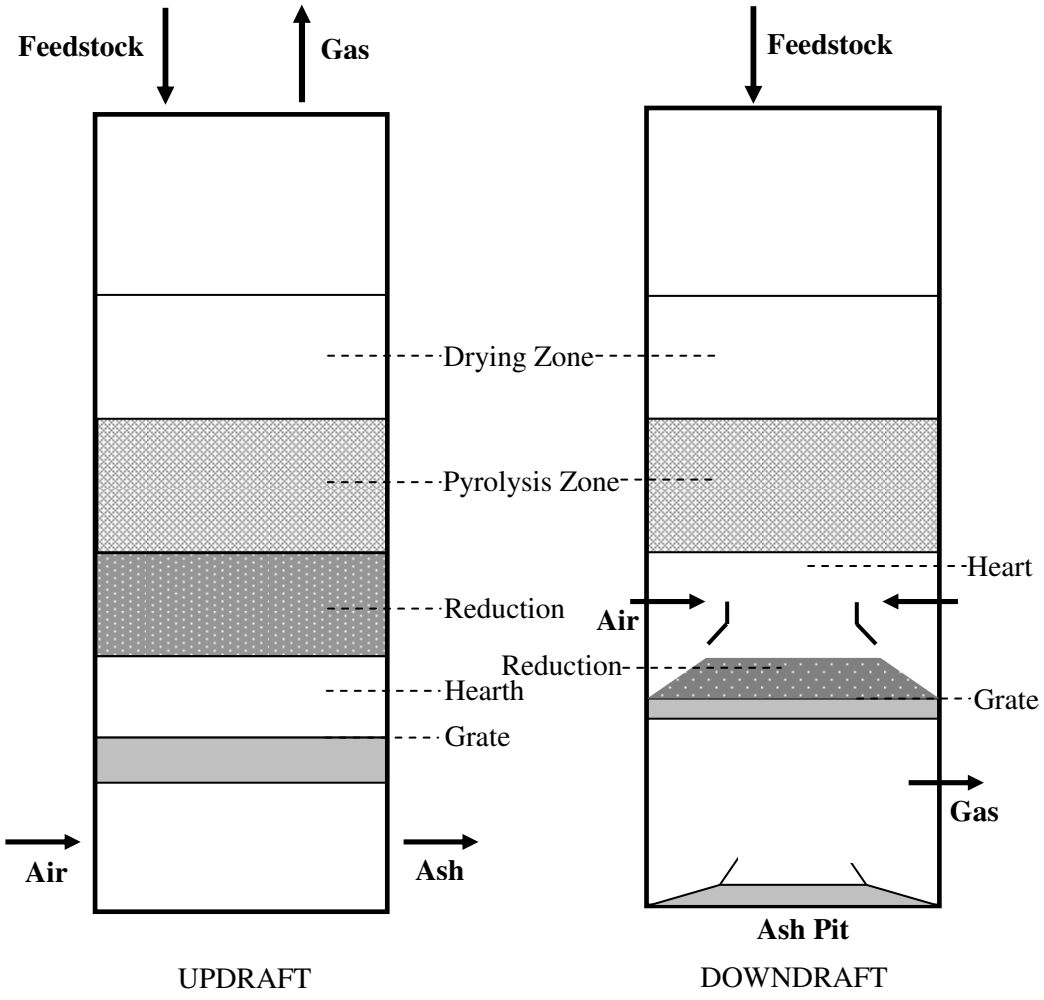


Figure 2.1: Fixed bed reactors.

In updraft gasifier, the feedstock is treated in the following sequence starting from the top: drying, pyrolysis, reduction, and combustion. As a consequence of the updraft configuration, the tar coming from the pyrolysis zone is carried upward by the following hot gas which results in the production of a gas with high tar content. Typically, the sensible heat of gas is recovered by means of a direct heat exchange with feedstock (Bridgwater 1994, 27).

In a downdraft gasifier, the air is introduced at the sides above the grate where the combustible gas is withdrawn under the grate (Juniper 2000). As a consequence of the downdraft configuration, pyrolysis vapours allow an effective tar thermal cracking.

However, the internal heat exchange is not efficient as in the updraft gasifier (Belgiorno 2003, 4).

Ragnar (2000) stated that in terms of reactor technology, fixed beds have a wide temperature distribution. This leads to drawbacks such as possibilities for hot spots with ash fusion, low specific capacity, long periods for heat-up, and limited scale-up potential. However, the advantages of this technology are high carbon conversion efficiency, the wide range of ash content in the feedstock and the possibility to melt the ash.

Fluidised bed reactors are the other commonly used gasifier for gasification process. Fluidised bed gasifiers are subdivided into *bubbling fluidised bed* and *circulating fluidised bed* as shown in Figure 2.2. The differences between bubbling fluidised bed and circulating fluidised bed are bubbling beds have relatively low gas velocities which results minimal solids to be transported, meanwhile circulating bed velocities are close to pneumatic flow therefore the entrained solids are recycled after passing a cyclone.

On contrary to fixed beds, fluidised bed gasifiers can offer higher throughput capabilities and greater fuel flexibility including the ability to handle low-density feedstock like undensified crop residues or sawdust (Johansson, Bodlund, and Williams 1989). However, gas quality is difficult to be controlled resulting in conflict between high reactions temperatures with good conversion efficiency and low melting points of ash components, e.g. alkali (Williams and Larson 1996, 159). Besides that, there is much more particulate carryover with a fluidised bed gasifier. The comparison between fixed bed and fluidised bed reactors is summarised in Table 2-6.

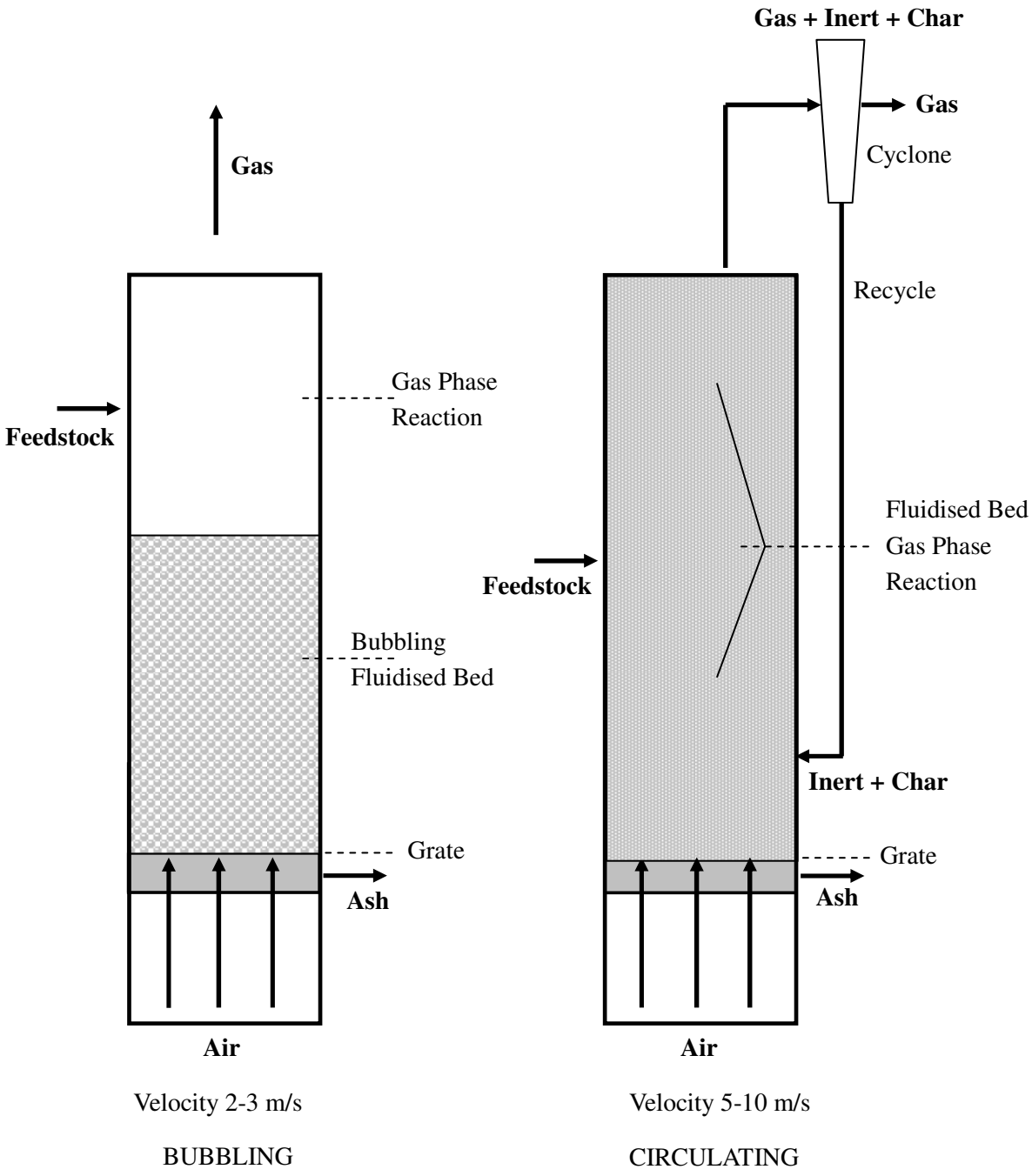


Figure 2.2: Fluidised bed reactors.

Table 2-6: Comparison of fixed bed and fluidised bed gasifier (Information taken from Ragnar 2000, 494).

Criteria	***Fixed Bed***
Technology	***Pros*** -Operation is much easier than fluidised bed ***Cons*** -Bad temperature distribution -Hot spots with exothermic reaction -Poor heat exchange -Possible ash agglomeration and clinker formation on grate -Channelling possible
Scale/Throughput	***Pros*** -Capacity is not limited by entrainment at high velocities ***Cons*** -Low specify capacity -High residence time of solids -Gasifier capacity is limited by gas low rates -Heat transport limits scale up
Start-up /Shutdown Behaviour	***Cons*** -Long period to heat up
Requirement of Educts	***Pros*** -High ash content feedstock possible -In-bed catalytic processing possible ***Cons*** -Only for catalysts that are deactivated very slowly -Close size specification required on feedstock -Large pellets (8-50mm) as uniform as possible -Feedstock fines must be handled separately (agglomeration)
Quality of Main Products	***Cons*** -Product gas contain tars, oil, phenols, and ammonia -Low exit gas temperature
Quality of Co-Products	***Pros*** -Low dust content in product gas -Low ash carry over
Efficiency of Conversion Rate	***Pros*** -High carbon conversion efficiency -Low ash carry over
Efficiency of Conversion Rate	***Pros*** -High carbon conversion efficiency -Specific oxygen consumption is low
Internal Load	***Pros*** -Do not require high gas flow rate
Environmental	***Pros*** -Molten slag possible ***Cons*** -No primary gas cleaning possible
Economy	***Cons*** -High investment for high load

Table 2-6 (continued)

Criteria	*Fluidised Bed*
Technology	***Pros*** **-**Good temperature distribution -No hot spots -Good heat exchange -Good gas solid mixing ***Cons*** -Operation can be more difficult than fixed bed
Scale/Throughput	***Pros*** -High specific capacity -Good scale up potential -High reaction rates, low residence time of solids ***Cons*** -Capacity is limited by entrainment at high velocities
Start-up / Shutdown Behaviour	***Pros*** -Easy start-up and shut down
Requirement of Educts	***Pros*** -Tolerates wide variations in fuel processing -Variety of particles size can be handled -Broad particle size distribution (ca. 0.02-50 mm) -High fines content acceptable ***Cons*** - In-bed catalytic processing hardly possible
Quality of Main Products	***Cons*** -Product gas contains tars, oil, phenols, and ammonia -Gas exit temperature is similar to bed temperature
Quality of Co-Products	***Cons*** - Higher particulates and dusts in the product gas than at fixed bed
Efficiency of Conversion Rate	***Pros*** -High carbon conversion efficiency
Internal Load	***Cons*** -High gas flow rate required for fluidisation
Environmental	***Pros*** -Primary gas cleaning possible ***Cons*** -Ash not molten
Economy	***Pros*** -Low investment

2.3 BIOMASS RESOURCES FOR GASIFICATION

There are variety types of biomass from energy crops, agricultural residues and waste, forestry waste and residues, to industrial and municipal wastes. Since palm shell is the feedstock for the gasification process in this research, this biomass is classified under agricultural residues and waste. It is essential to understand the properties of the biomass because it might have significant effect on the performance of the gasifier and also its downstream process.

2.3.1 Biomass Classification

A variety of biomass resources can be used to convert energy and it is categorised into four main types (Ni et al. 2006, 461):

(i) Energy crops: herbaceous energy crops, woody energy crops, industrial crops, agricultural crops and aquatic crops.

(ii) Agricultural residues and waste: crop waste and animal waste.

(iii) Forestry waste and residues: mill wood waste, logging residues, trees and shrub residues.

(iv) Industrial and municipal wastes: municipal solid waste (MSW), sewage sludge and industry waste.

Balat et al. (2009, 3148) mentioned that the chemical structure and basic organic components in biomass are extremely important in the development of processes for producing derived fuels and chemicals.

Biomass as clean components can be understood as any hydrocarbon material which mainly consists of carbon, hydrogen, oxygen and nitrogen (Yaman 2004, 653). The major organic components of biomass can be classified as cellulose, hemicelluloses and lignin.

Cellulose is a remarkable pure organic polymer, consisting solely of units of anhydroglucose held together in a giant straight chain molecule (Hashem et al. 2007). Cellulose is a homopolysaccharide composed of β-D-glucopyranose units linked together by (1→4)-glycosidic bonds (Mohan, Pittman and Steele 2006).

Hemicelluloses are complex polysaccharides that take place in association with cellulose in the cell wall, but unlike cellulose, hemicelluloses are soluble in dilute alkali and consist of branched structures, which vary considerably among different woody and herbaceous biomass species (Yaman 2004, 653). Many of them have the general formula $(C_5H_8O_4)_n$.

Lignins are highly branched, substituted, mononuclear aromatic polymers in the cell walls of certain biomass, especially woody species, and are often bound to adjacent cellulose fibers to form a lignocellulosic complex (Yaman 2004, 653). This complex and the lignins alone are often quite resistant to conversion by microbial systems and many chemical agents.

2.3.2 Properties of Biomass

Selecting the type of biomass as gasification feedstock is essential since the properties of biomass can cause significant effect on the performance of the gasifier and also its downstream process. The biomass properties that can influence the effect of biomass gasification are the moisture content, calorific value, proportions of fixed carbons and volatiles, ash or residue content, alkali metal content and particles sizes of the biomass.

(i) Calorific value

Calorific value of a material can be defined as the energy content, or heat value, released when burnt in air. The moisture content of the feedstock will give effect to the calorific value since the calorific value is indirectly proportional to the moisture content of the feedstock.

(ii) Moisture content

Biomass feedstock with high moisture content of greater than 30% will lead to poor ignition and reduces the calorific values of the product gas. This is because biomass with high moisture content reduces the temperature achieved in the oxidation zone, and therefore resulting in incomplete cracking of tars released from the pyrolysis zone and high tar content in the gas (McKendry 2002b, 56).

The increased levels of moisture and the presence of carbon monoxide, CO products by the water gas shift reaction, Equation (2.4) will result in an increase of hydrogen, H_2 content of the gas. Since the steam methane reforming reaction, Equation (2.5) is a reversible reaction, therefore the increase of H_2 content will result in an increase of methane, CH_4 content. The gain in H_2, and CH_4 of the product gas does not however compensate for the loss of energy due to the reduced CO content of the gas and

therefore gives a product gas with a lower calorific value (McKendry 2002b, 56). Therefore, it is crucial to evaporate the additional moisture in order for gasification or combustion to take place. It is also reported by several authors (Agarwal, and La Nauze 1989), (Saastamionen 1994), and (Werther et al. 1995) that the presence of moisture greatly delay the release of the moisture volatiles in brown coal, wood chips, wood logs, and sewage sludge. Further, the quality of flue gas formed during the combustion of high moisture content which eventually leads to large dimensions of the equipment for flue gas treatment (Werther et al. 2000, 4).

(iii) Proportions of fixed carbons and volatiles

Fixed carbon (FC) is refer to the mass of the carbon found in the biomass after the biomass is heated and the volatiles has expelled meanwhile volatiles matter (VM) is refer to volatile compounds released including moisture as gas when biomass heated to a temperature of 950 ºC. The VM and FC contents in biomass are important as they provide a measure of ease with which the biomass can be ignited and subsequently gasified, or oxidised, depending on how the biomass is to be utilised as an energy source (McKendry 2002a, 42).

(iv) Ash and Residue Content

The ash presents in or on the surface of the biomass is made up of inorganic constituents, such as organically bound cations, inorganic salts and mineral (Arvelakis and Koukios 2002). The oxidation temperature is often above the melting point of the biomass ash, leading to clinkering or slagging problems in the hearth and subsequent feed blockages (McKendry 2002b, 56). Ash will produce eutectic mixtures with low melting points if the ash content is above 5% and containing high alkali oxides and salts. For the gasification of biomass with high ash content using catalyst, it is necessary to separate the catalyst from the ash in biomass. One can follow the way recommended by Bridgwater (1994, 29) with the use of two separate reactors (secondary-bed reforming of tar and an ash separator) in between the reactors or a dual bed for ash and char separation mentioned by Asadullah et al. 2004, 99.

(v) Alkali Metals

The alkali metals content of the biomass and its quantities are very important in any thermo-chemical conversion processes. This is because the chemical composition of the ash determines the physical properties of the material such as softening, melting points, or vaporisation points (Stevens 2001).

(vi) Particle Size

It is essential to perform screening on the biomass feed prior used to remove oversize particle which could easily lead to bridge in the gasifier meanwhile smaller particles size could tend to clog the available air voidage which consequently built high pressure drop and subsequently leading to a more severe problem such as shutdown of the gasifier.

In Table 2-7, the proximate and ultimate analyses of several types of biomass are presented. The proximate analysis includes the determination fixed carbon, volatiles, ash, and high heating value (HHV) meanwhile the ultimate analysis includes the percentage of carbon, hydrogen, oxygen, nitrogen and sulphur. It is observed that biomass is group from wood, bark, energy crops, processed biomass, to agricultural.

Table 2-7: Proximate and ultimate analysis of several types of biomass ((Gaur and Reed 1998) and (Islam et al. 1999)).

Biomass	***Proximate Analysis***				***Ultimate Analysis***				
	Fixed Carbon (%)	Volatiles (%)	Ash (%)	HHV (kJ/g)	C (%)	H (%)	O (%)	N (%)	S (%)
Wood									
Beech	-	-	0.65	20.38	51.64	6.26	41.45	0.00	0.00
Black Locust	18.26	80.94	0.80	19.71	50.73	5.71	41.93	0.57	0.01
Douglas Fir	17.70	81.50	0.80	21.05	52.30	6.30	40.50	0.10	0.00
Hickory	-	-	0.73	20.17	47.67	6.49	43.11	0.00	0.00
Maple	-	-	1.35	19.96	50.64	6.02	41.74	0.25	0.00
Pinus Pinaster	17.17	82.54	0.50	18.40	49.25	5.99	44.36	0.06	0.03
Poplar	-	-	0.65	20.75	51.64	6.26	41.45	0.00	0.00
Red Alder	12.50	87.10	0.40	19.30	49.55	6.06	43.78	0.13	0.07
Redwood	16.10	83.50	0.40	21.03	53.50	5.90	40.30	0.10	0.00
Western Hemlock	15.20	84.80	2.30	20.05	50.40	5.80	41.10	0.10	0.10
Yellow Pine	-	-	1.31	22.30	52.60	7.00	40.10	0.00	0.00

White Fir	16.58	83.17	0.25	19.95	49.00	5.89	44.75	0.05	0.01
White Oak	17.20	81.28	1.52	19.42	49.48	5.38	43.13	0.35	0.01
Madrone	12.00	87.80	0.20	19.51	48.94	6.03	44.75	0.05	0.02
Mango Wood	11.36	85.64	2.98	19.17	46.24	6.08	44.42	0.28	-
Bark									
Douglas Fir Bark	25.80	73.00	1.20	22.10	56.20	5.90	36.70	0.00	0.00
Loblolly Pine Bark	33.90	54.70	0.40	21.78	56.30	5.60	37.70	0.00	0.00
Energy Crops									
Eucalyptus Camaldulensis	17.82	81.43	0.76	19.42	49.00	5.87	43.97	0.30	0.01
Casuarina	19.58	78.58	1.83	18.77	48.50	6.04	43.32	0.31	0.00
Poplar	16.35	82.32	1.33	19.38	48.45	5.85	43.69	0.47	0.01
Sudan Grass	18.60	72.75	8.56	17.39	44.58	5.35	39.18	1.21	0.01
Processed Biomass									
Plywood	15.77	82.14	2.09	18.96	48.13	5.87	42.46	1.45	0.00
Agricultural									
Peach Pits	19.85	79.12	1.03	20.82	53.00	5.09	39.14	0.33	0.05
Walnut Shells	21.16	78.28	0.56	20.18	49.48	5.71	43.35	0.21	0.01
Almond Prunnings	21.54	76.83	1.63	20.01	51.30	5.27	4.09	0.66	0.01
Palm Shells	20.30	68.80	2.30	20.11	55.35	6.43	38.01	0.37	-
Black Walnut Prunnings	18.56	80.69	0.78	19.83	49.80	5.82	43.23	0.22	0.01
Corncobs	18.54	80.10	1.36	18.77	46.58	5.87	45.46	0.47	0.01
Wheat Straw	19.80	71.30	8.90	17.51	43.20	5.00	39.40	0.61	0.11
Cotton Stalk	22.43	70.89	6.68	18.26	43.64	5.81	43.87	0.00	0.00
Corn Stover	19.25	75.17	5.58	17.65	43.65	5.56	43.31	0.61	0.01
Sugarcane Bagasse	14.95	73.78	11.27	17.33	44.80	5.33	39.55	0.38	0.01
Rice Hulls	15.80	63.60	20.6	14.89	38.30	4.36	35.45	0.83	0.00
Pine Needles	26.12	72.38	1.50	20.12	48.21	6.57	43.72	-	0.00
Cotton Gin Trash	15.10	67.30	17.60	16.42	39.59	5.26	36.36	2.09	0.00

2.3.3 Biomass Palm Shells

Biomass is potentially an attractive feedstock for providing potential source of hydrocarbons with almost zero net CO_2 emission to the atmosphere environment. The efficient utilisation of biomass as a source of clean energy and chemicals has attracted much research attention in recent years amid to fossil fuel energy crisis as well as clean energy drive.

Oil palm, or also known as *Elaeis guineensis* which belongs to the family of Palmae was initially introduced to Sumatera and Malaya area in early 1900s (Shuit et al. 2009,

1226). Originated from South Africa, it is cultivated in all tropical area of the world and it becomes one of the main industrial crops (Yong et al. 2007, 5694). The oil palm fruit is reddish in colour and about the size of a large plum, but it grows in large bunches as shown in Figure 2.3. Each fruit consists of a single seed (the palm kernel) and surrounded by a soft oily pulp. Oil is extracted from both pulp of the fruit, which can be made into edible oil, and kernel, which is used mainly for soap manufacturing (Yong et al. 2007, 5694). Oil palm is a multi-purpose plant and also a prolific producer of biomass as raw materials for value-added industries (Basiron and Simeh 2005). For example, fresh fruit bunch contains only 21% palm oil, while the rest 6-7% kernel, 14-15% fiber, 6-7% shell and 23% empty fruit bunch (EFB) are left as biomass (Umikalsom et al. 1997).

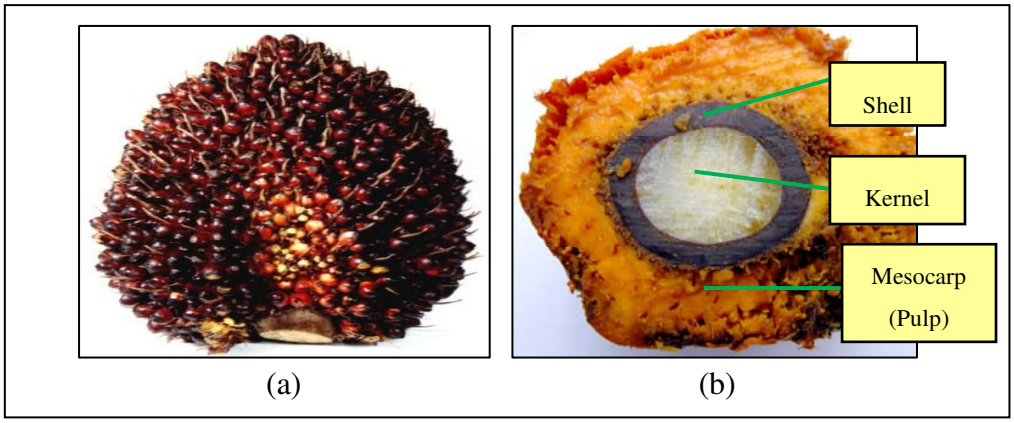


Figure 2.3: (a) Fresh oil palm fruit bunch (b) Longitudinal section of oil palm fruit.

In this research, biomass palm oil is selected as gasification feedstock in view of the fact that it is one of the favourable bioenergy sources due to the growing global demand for edible oil which has resulted in oil palm to become today world's largest source of edible oil with 38.5 million or 25% of the world edible oil and fat production as shown in Figure 2.4 (MPOC 2008). Thus, oil palm has now become a major economic crop which triggered expansion of plantation area in Malaysia and Indonesia. In year 2006, Malaysia is the second largest producer of palm oil with 15.88 million tonnes or 43% of the total world supply as shown in Figure 2.5 (U.S. Department of Agriculture 2007). Indonesia is the world's largest producer of palm oil with 15.9

million tones of oil or 44% of the total world supply. In 2007, productive oil plantations in Malaysia are 4.3 million hectares, a 3.4% increase from year 2006 which stood at 4.2 million hectares (MPOB 2007).

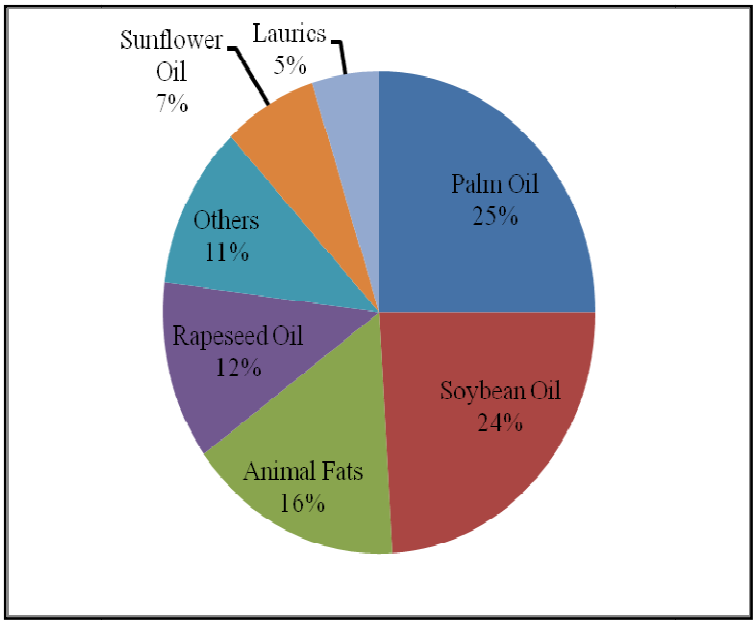


Figure 2.4: World's oil production in 2007 (MPOC 2008).

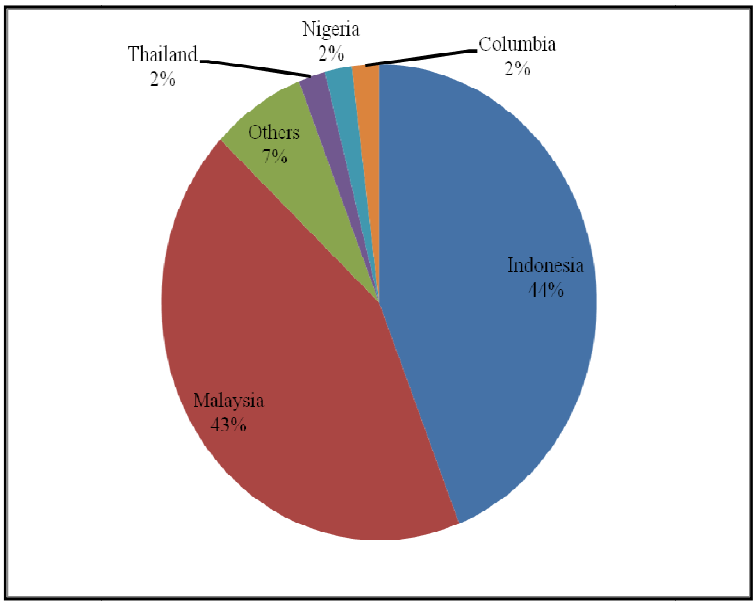


Figure 2.5: World producers of oil palm in 2006 (oil with 15.88 million tonnes or 43% of the total world supply) (U.S. Department of Agriculture 2007).

As the result, palm oil wastes (empty fruit bunches (EFB), kernel, fibre, and shell) from palm oil production has increased markedly. It is reported in Malaysia that more than 7 million tonnes of EFB, 4.5 million tonnes of fibre, and 1.9 million tonnes of

shell are generated as solid wastes, at an increase of 5% annually (Yang et al. 2004). Due to huge amount of biomass generated yearly, countries such as Malaysia and Indonesia have the potential to utilise the biomass effectively to other value products. For examples, the utilisation of empty fruit bunches (EFBs) to produce bioplastic, EFBs incinerated for soil conditioner, fronds converted to pulp, and palm fibres to be used as fillers in thermoplastics and thermoset composites (Shuit et al. 2009).

Besides that, oil palm biomass can contribute a positive and promising prospect as a source of renewable energy with regards to the current state of energy crisis with the price of crude petroleum hitting record high recently and also high calorific energy content as shown in Table 2-8.

Table 2-8: Calorific values of oil palm biomass (Subramaniam, Chow, and Ma 2003).

Oil Palm Biomass	***Calorific Values (kJ/kg)***
EFBs	18,795
Kernels	18,884
Fibres	18,795
Shells	20,093

From Table 2-7, it is observed that the fixed carbon for palm shells is relatively higher and the volatiles content is only slightly lower compared with wood. As it is commonly known that wood can be easily ignited, therefore it can be concluded based on the fixed carbon and volatiles content of the palm shells that this biomass can also be easily ignited and subsequently gasified, or oxidised as an energy source. It is found that the ash content in palm shells is lower than 5% which gives a lower tendency in producing eutectic mixtures with low melting points which could lead to clinkering or slagging problems in the hearth and subsequent feed blockages (McKendry 2002b, 56). The high heating value (HHV) of palm shells is comparable to the listed biomass in Table 2-7.

Presently, the most conventional way of handling this biomass is to burn them with

energy recovery (combustion) or for landfilling (Ghani et al. 2009, 259). Both these methods do not contribute to net amount of carbon in the atmosphere as carbon is assimilated during plant growth resulting secondary pollution problems.

Biomass used in solving these methods is to implement biomass gasification technology for high efficiency power generation, heat and/or combined heat and power (CHP) applications. It can be used for the production of liquid fuels and chemical via synthesis gas (syngas).

However, gas cleaning is the bottleneck in advanced gas utilisation that limits the deployment of the use of biomass for electricity production in a gas turbine (Kaltschmitt and Rösch 1998). Gas turbine are highly encouraged to be chosen over gas engine for power generation as it is capable of producing large amounts of useful power for a relatively small size and weight, mechanical life is long and the corresponding maintenance cost is relatively low as motion of all its major components involve pure rotation instead of reciprocating motion as in a piston engine, and wide variety of fuels can be utilised (Langston and Opdyke 1997). Gas turbines are highly sensitive to the quality of gas, which means only extremely low levels of contaminants, principally tars, alkali metals, sulphur and chlorine compounds can be tolerated. These contaminants can cause erosions, emission of pollutants such as nitrogen oxides (NO_x) and sulphur oxides (SO_X), hot corrosion, clog filters and deposits internally (Giampaolo 2005). Therefore, the efficiency of a gas cleaning technology step is fundamental to the successful operation of power plants and also clearly shows that gas cleaning technologies to be very important in biomass gasification process. So far only limited types of biomass such as woody and straw feedstock have been successfully been carried out in biomass gasification process and no studies were conducted on biomass palm shells feedstock especially on this process before.

2.4 STATE OF THE ART FOR GAS CLEANING

One of the main hurdles of using syngas is the requirement to clean the gas prior to conversion to energy and is vital to be applied for the prevention of erosion, corrosion, and environmental problems in downstream equipment. Most of the technologies selected for the syngas cleanup system are mainly oriented for gasification of coal or other petroleum compounds. Therefore, it is a crucial step to have a deep understanding on biomass derived syngas production of an acceptable level of quality and cleanliness for gas turbine application since turbines are highly sensitive to the quality of gas as compared to engine, which means only extremely low levels of contaminants, principally tars, alkali metals, sulphur and chlorine compounds can be tolerated.

Typical gas turbines must be adapted to the low heating value (LHV): for an easier start up, the burners must allow dual fuel operation and longer combustion chambers are necessary to improve the control of CO emissions ((Zarfolin 2005) and (Becker and Schetter 1992)). Table 2-9 shows the gas quality requirement for engine and gas turbine.

Table 2-9: Gas quality requirements for engine and gas turbine (Belgiorno et al. 2003, 8).

	Engine	***Gas Turbine***
Low Heating Value, LHV (MJ/Nm^3)	>4	>4
Particulate (mg/Nm^3)	<5-50	>5-7
Tars (g/Nm^3)	<0.5	<0.1-0.5
Alkali Metals (ppm)	<1.2	<0.2-1

Gas cleanup systems can take place either during or after the gasification process. Systems producing either fuel or synthesis fuel or synthesis gas must deal with the cleanup of five primary contaminants including particulates, alkali compounds, tars, nitrogen containing compounds and sulphur.

2.4.1 Particulates

Particulates originate from the ash of the feedstock, dust, unconverted carbon (in product gas from low temperature gasification), soot (typically for high temperature oxygen-blown gasification), and carry over bed material in the case of fluidised bed gasifiers (Boerriigter and Rauch 2005). The technologies used for the removal of particulates are cyclones, barrier, filters, electrostatic filters (ESP) and solvent scrubbers. These methods mentioned are commonly practised in industrial for the removal of this contaminant and also proven to be efficient.

2.4.2 Nitrogen Containing Compounds

The removal of ammonia from the product gas is necessary since the ammonia will be converted to NO_x during combustion. Nitrogen containing compounds all exist in the vapour phase and will therefore pass through all particulate removal devices. There are four conventional ways of approaching the problems of NO_x emissions, any of which may be used singly or in combination (Bridgwater 1995, 642a): (1) Reduction of the formation of NO_x by limiting fuel-bound nitrogen in the feedstock through careful selection of biomass types and/or blending, (2) Wet scrubber, which removes ammonia and other soluble nitrogen compounds (3) Use of low NO_x combustion techniques to minimise thermal NO_x production (4) Use of selective catalytic reduction (SCR) at the exhaust of the engine or turbine. SCR involves a reaction between ammonia and NO_x to form nitrogen and water.

Due to the fact that palm shells have very low nitrogen content (~0.37%), therefore it can be concluded that it is likely to produce very minimal NO_x and will not be consider as a major problem during the gasification process.

2.4.3 Sulphur

Sulphur is not generally considered to be a problem, since biomass feeds have very low sulphur contents. For those feedstock's containing high sulphur levels, the sulphur containing species will be converted to sulphur oxides (SO_x) when the gas is burned.

Wet scrubbers are commercially available for SO_x removal and are well proven commercially (Stevens 2001).

2.4.4 Chlorine

Chlorine is another potential contaminant, which can arise from pesticides and herbicides as well as in waste materials. Chlorine and its compounds can be removed by absorption in active material either in the gasifier or in a secondary reactor, or by dissolution in a wet scrubbing system. Table 2-10 shows a summary of the comparison between the advantages and disadvantages of different gas cleaning technologies.

Table 2-10: Advantages and disadvantages of different gas cleaning technologies.

System	***Advantages***	***Disadvantages***
Thermal Cracking	Simple control Low Cost	LHV losses Low efficiency
Catalytic Cracking	LHV unchanged Easily to be upgraded No gas cooled	Catalyser cost Difficult control
Scrubber	Easy control Air pollution	LHV losses Gas is cooled Wastewater production

From the chemical analysis of palm shells obtained from Islam et al. 1999, 74 and Azali et al. 2005, 74, there is no chlorine found in the biomass. Therefore, chlorine is not considered to be an attribute problem in the gasification process.

2.4.5 Tars

Tars are also known as organic contaminants which consist of a mixture of aromatic and polyaromatic hydrocarbons. The tar is formed due to molecular bonds break during heating of biomass. The smallest molecules are gases, and the larger molecules are called tars. Tars are classified into primary, secondary, and tertiary tars. Primary tars, which are always fragment of the original material, can react to become secondary tars by furthered reactions at the same temperature and tertiary tars at higher

temperature (Basu 2006, 84).

The impact of tars in biomass gasification systems is that tars can condense in exit pipes and on particulate filters leading to blockages and clogged filters, varied impacts on other downstream processes, clogging fuel lines, and injectors in internal combustion engines, luminous combustion and erosion from soot formation occurring in pressurised combined-cycle systems where are product gases are burned in a gas turbine (Dayton 2002, 1).

Tars can be removed or destroyed from the product gas by chemical and physical methods. Chemical methods destroy the tar, converting it to smaller molecules meanwhile physical methods only remove the tar yielding a tar waste stream. Typical examples for chemical methods are catalytic cracking, thermal cracking, plasma reactors (Pyroarc, Corona, Glidarc) and use of catalytic bed materials (Basu 2006, 84). Cyclones, filters (baffle, fabric ceramic, granular beds), electrostatic precipitators, and scrubbers are examples of the physical methods. Thermal processes raise the temperature of the producer gas (>1000ºC) to levels that "crack" the heavy aromatic tar species into lighter and less problematic species, such as hydrogen, carbon monoxide, and methane. Catalytic processes can operate at much lower temperature (600-800ºC) than thermal processes, alleviating the need for expensive alloys for reactor construction. Dayton (2002) carried out an overview of the different catalysts that had been studied and how they had been implemented. He evaluated as well the future potential of this gas cleaning technology.

Previous studies were carried out on different feedstock (peat, coal, wood chips) using air as gasifying agent in fluidised bed reactor ((Kurkela and Ståhlberg 1992) and (Leppälahti and Kurkela 1991)). Tar concentration is mainly function of gasification temperature, and tar decreases as temperature increases (Bridgwater 1995, 641). However, tars formed in pyrolysis that is thermally cracked will be converted to refractory tars, soots, and gases. Besides that, tar level and characteristics are also

dependent on the feedstock. It is reported that tar production in wood gasification is much greater than in coal or peat gasification and the tars tend to be heavier, become more stable aromatics (Diebold et al. 1994, 230). These may partly react to give soot which can block filters, a problem apparently peculiar to biomass gasification. And also, the design of the gasifier plays an important role to destruct tars and the hydrocarbons released during the pyrolysis stage of the gasification (McKendry 2002, 57).

2.4.6 Alkali Compounds

The alkali metals exist in vapour phase at moderate temperature of 700ºC due to the eutectic point of the sodium and potassium salts in the ash material (Stevens 2001). Therefore, the removal of the alkali compounds is more difficult compared to particulates since the vaporised alkali compounds will remained in the product gas at high temperature. As the result, the alkali vapors cannot be readily removed from the hot gas stream by simple filtration. Since the maximum temperature that is considered to be effective for condensing metal species is of ~600°C, thus the condensed alkali metals will entrain on the solids and be removed at the particulate removal stage (Bridgwater 1995, 642). Alkali compounds exceeding the gas turbine requirements (<1 ppm) will result in high temperature corrosion of turbine blades, and stripping off their protective oxide layer.

However, this contaminant is not as problematic compared with tar as most technologies on the removal of alkali compounds such as cyclonic filters, barriers filters, electrostatic filters, and wet scrubbers are quite established and easily available commercially.

2.5 TAR CLASSIFICATION

Tar is the main concern in terms of contaminants produced in the biomass gasification system as it is a major nuisance which is associated to problems such as leading blockages in exit pipes, clogged particulate filters and also caused various impacts to

the downstream processes. Furthermore, these tars are dangerous because of its carcinogenic character, and they contain significant amounts of energy that can be transferred to the fuel gas as H_2, CO, CH_4 and others (Abu et al. 2004, 6911). And also, concentrations of tars greater than 0.5 g/Nm^3 can damage or lead to unacceptable levels of maintenance of turbines (Belgiorno et al. 2003, 8). Therefore, a suitable method is required in reducing and eliminating tars produce in gasification process and also optimising the operating conditions to produce the least amount of tars.

Tar composition is strongly dependent on the operating conditions of the gasification process. Stevens (2001) mentioned that the tar varies in composition from primary oxygenated pyrolysis products at lower temperatures to high molecular weight, deoxygenated products for those that have experienced severe reaction conditions as shown in Figure 2.6. As biomass is heated, it dehydrates and then volatilises as its thermal decomposition to form permanent gases, or it can undergo dehydration, condensation and polymerisation reactions that result in tar formation (Stevens 2001).

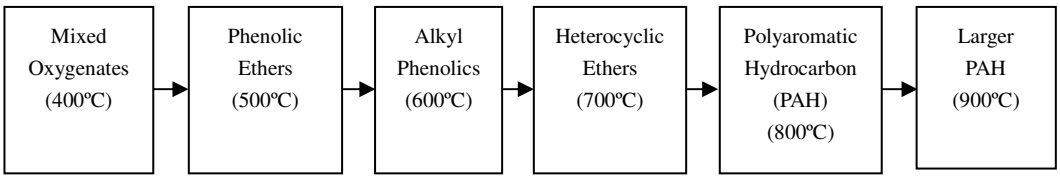


Figure 2.6: Formation of tar in different temperature in gasification process (Stevens 2001).

Several researchers have classified tars into different classes and study the behaviour among these classes which had been reported in the literature. Milne et al. (1998) classified tars in three groups depending on the reaction regimes as shown in Figure 2.7. These three groups are: “primary products” which are characterised by cellulose-derived, hemicelluloses-derived and lignin-derived products, “secondary products” which are mainly methyl derivatives of aromatic compounds, “condensed tertiary products” which are PAH without substituent groups. Primary products are destroyed before the tertiary products appear.

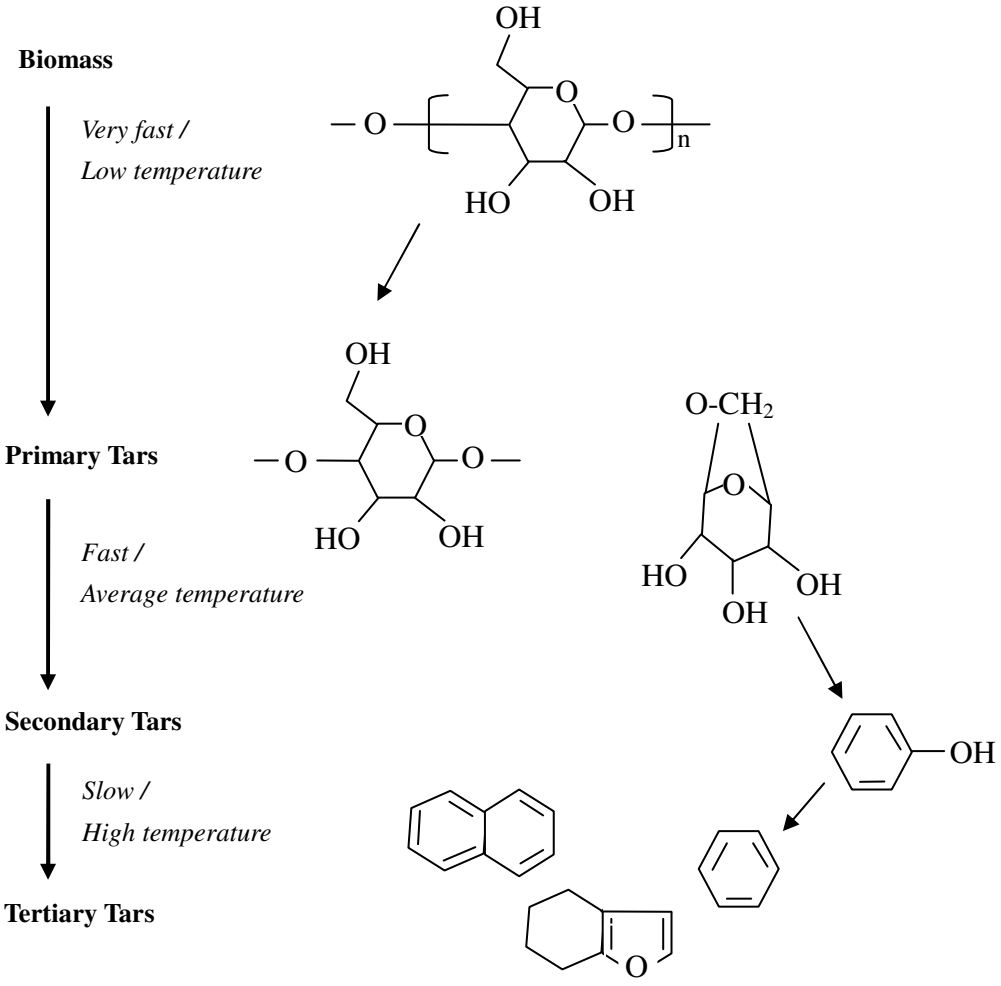


Figure 2.7: Tar classes as reported by Milne, Evans and Abatzoglou (1998).

According to van Paasen and Kiel (2004, 4), the impact of tar formation on the performance of downstream processes mostly is not related to the lump-sum tar content (expressed, e.g. in g/m_n^3 "tar"), but problems are merely caused by specific fractions or tar compounds. Therefore, much emphasis has been given to the determination of the tar composition by measuring individual tar compounds. Based on the behaviour of the tar compounds in downstream processes, the classification system was derived as presented in Table 2-11.

Table 2-11: Tar classification system (Devi 2005, 36).

Class	***Name***	***Description***	***Tar Compounds***
1	GC-undetectable	Very heavy tars that can condense at high temperature even at very low concentrations	Biomass fragments, heaviest tars (pitch)
2	Heterocyclic Aromatics	Tars containing hetero atoms, high water solubility due to their polarity	Pyridine, Phenol, Cresol, Quinoline
3	Light Aromatics (1 ring)	Light hydrocarbons that are not important in condensation and water solubility issues	Xylene, Styrene, Toluene, Ethylbenzene (excluding benzene)
4	Light Polyaromatics	2-3 rings polyaromatic hydrocarbons (PAH) compounds which condense at relatively high concentration and intermediate temperatures	Phenanthrene, Anthracene, Naphthalene, Indene, Biphenyl
5	Heavy Polyaromatic	4-7 rings PAH compounds that condense at relatively high temperature at low concentrations	Fluoranthene, Pyrene, Chrysene, Benzo-fluoranthene, Benzopyrene, Perylene.

The principle of classification by Corella et al. (2000) lumped all the tar species into 6 groups namely benzene, 1-ring compound, naphthalene, 2-ring compounds, 3- and 4-ring compounds and phenolic compounds. The authors also proposed a reaction on network suggesting the inter-dependency of each group.

Another classification was presented by Pérez et al. (1997) and Corella et al. (2002) who divided tars into two groups, namely “easy to destroy” which are characterised by more reactive tar species and “hard to destroy” which are mainly less reactive tar species.

Among all the mentioned tar classifications, the most preferred classification of tar to be applied in this research is that by Devi (2005, 36). This is because this classification is mainly based on solubility and condensability of different tar compounds, rather than reactivity of the compounds (Devi 2005, 35). Condensation behaviour is important, for example, with respect to fouling in gas cooling or gas cleaning equipment. The oxygenated or heterocyclic tar compounds containing O and/or N atoms like phenol are highly water soluble due to their high polarity that may lead to hazardous wastewater, which could result in high disposal/processing cost for low-temperature gas cleaning systems (Kiel et al. 2004, 19).

2.6 CATALYTIC CRACKING

Catalytic cracking is used as the gas cleaning technologies specifically for the removal of tar in biomass gasification process using palm shells feedstock in this research. Catalytic cracking is selected to be used rather than thermal cracking as this method does not required as high temperature compared with thermal cracking which could save operating cost in this system and also the cracking reaction increases the yield of improved quality products at a lower temperature.

Tar decomposition mainly occurs due to cracking, steam and dry reforming reaction. In this research, catalytic cracking is selected as the hot gasification gas cleaning for this research. The catalyst used for catalytic cracking is to enhance the decomposition of tar and heavier hydrocarbons formed by incomplete gasification of pyrolysis products, as shown below:

Cracking:

$$pC_nH_x \rightarrow qC_mH_y + rH_2 \qquad (2\text{-}8)$$

Among the possible gas cleaning methods, catalytic hot gas cleaning is the most recommended because it completely destroys the tar, as well as the ammonia, rather

than transforming them to a waste liquid stream that is very difficult to dispose (Corella, Toledo, and Padilla 2004, 2433). Catalyst cracking has been of interest since the middle of 1980s due to the advantages of converting tar into useful gases and adjusting the compositions of product gases (Han and Kim 2006). The advances in this area have been driven by the need of a tar-free product gas production from the gasification of biomass, since the removal of tars and the reduction of the methane content increase the economic viability of the biomass gasification process (Sutton et al. 2001). However, there are many technical and economic reasons such as thermal efficiency, environmental emissions compliance, non-condensible hydrocarbon gas removal, tar or effluent treatment cost to justify catalytic cracking of tars before cooling. For example, if hot chemical conversion processes are adopted for gas conditioning, hot gas conditioning, hot removal of particulates and aerosols must be included as these constituents can cause catalyst fouling and poisoning and deactivation in the cracking operations which results in excessive compressor erosion (Milne et al. 1998, 41). Since no studies have been done on the catalytic cracking on the tar produced from gasification of palm shells, therefore the catalyst selection for tar cracking should satisfy the following criteria listed by Sutton et al. (2001, 156):

(i) Catalyst must be effective in the removal of tars,

(ii) Able to resist deactivation from carbon fouling and sintering,

(iii) Easily generated,

(iv) Have resistant to abrasion and attrition,

(v) Cost should be cheap, and

(vi) Catalysts must be capable of reforming methane and providing syngas ratio for the intended process if the desired product is syngas.

The catalyst can either be added directly to the biomass prior to gasification or placed in a secondary reactor downstream from the gasifier in which the latter method can operated under different conditions from the gasification unit.

2.7 ZEOLITES

Zeolites are selected as a catalyst for hot gas clean up in the fixed bed reactor in this research since this catalyst group have the potential to eliminate tars from fuel gas (Abu et al. 2004, 6915). However, very limited research has been performed to evaluate zeolites for tar removal applications (Buchireddy et al. 2010) and no studies have been carried out using this catalyst on palm shells gasification. The advantages of using this catalyst compared with amorphous catalysts are related to their acidity, better thermal/hydrothermal stability, better resistance to nitrogen and sulphur compounds, tendency toward low coke formation, and easy regenerability (Sherzer and Gruia 1996). Other than that, zeolites are easily available, cheap, and has experience gained using this catalyst in FCC units, which offers better practical insight (Buchireddy et al. 2010). Nonetheless, the main disadvantage is the coke formation which results in these catalysts to rapid deactivation (Abu et al. 2004, 6915). Zeolites are commonly used as a catalyst for fluid catalytic cracking (FCC) units in oil refineries in oil industries to increase the motor octane of gasoline, increase the total liquefied petroleum gas (LPG) and increase the olefin content of the fraction (Sadeghbeigi 2000). To describe some general information:

- ***Structures***

Zeolites are microporous, aluminosilicate minerals and occur in nature. The elementary building units of zeolites are SiO_4 and AlO_4 tetrahedrons. Adjacent tetrahedral are linked at their corners via a common oxygen atoms, and hence a structurally distinct three-dimensional framework exist (Weitkamp 2000, 176). This is apparent from the building principle that the net formulae of the tetrahedrons as there are chemical compounds such as SiO_2 and AlO_2^-, where the alumino-silicate is negatively charged and attracts the positive cations that reside within. Zeolite framework consists of channels, channel intersections and/or cages with dimensions from ca. 0.2 to 1 nm (Weitkamp 2000, 176). Inside these voids are water molecules and small cations which compensate the negative framework charge. Therefore, the chemical composition of a zeolite can be represented by the following formula (Weitkamp 2000, 176):

$$A^{m+}_{y/m}\left[(SiO_2)_x.(AlO_2^-)_y\right]zH_2O \qquad (2\text{-}9)$$

where *A* is a cation with the charge *m, (x+y)* is the number of tetrahedral per crystallographic unit cell and *x/y* is the so-called framework silicon/aluminium ratio n_{Si}/n_{Al} (or simply Si/Al).

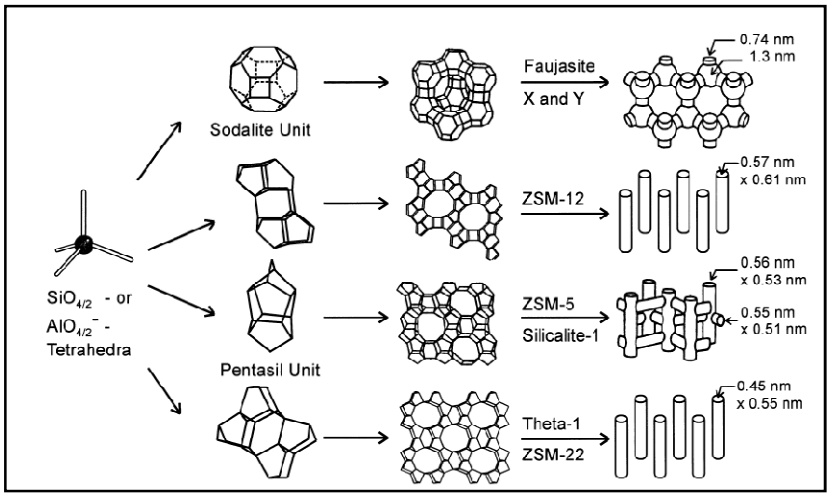


Figure 2.8: Structures of four selected zeolites
(from top to bottom: faujasite or zeolites X, Y: zeolite ZSM-12; zeolite ZSM-5 or silicalite-1: zeolite Theta-1 or ZSM-22) and their micropore systems and dimensions (Weitkamp 2000, 177).

- ***Applications of Zeolite in Industries***

There are three main uses for zeolites in industry, which can be used as catalysis, gas separation and ion exchange.

In catalysis, zeolites are useful for several reactions involving organic molecules such as cracking, isomerisation and hydrocarbon synthesis. Besides that, zeolites also promote a diverse range of catalytic reactions including acid-based and metal induced reactions, acts as an acid catalyst and are used as supports for active metals or reagents (*Zeolite applications* 2009a).

Furthermore, zeolites can confine molecules in small spaces which allow changes in their structure and reactivity (*Zeolite applications* 2009b). The unique microporous nature of zeolites causes the shape and size of a particular pore system to exert a steric influence on the reaction which gives it an ability to control the access of reactants and

products (Win 2007, 38). Hence, they are known as shape-selective catalysts. In petrochemicals industry, synthetic zeolites are widely used as catalyst for fluid catalytic cracking and hydro cracking.

In gas separation, zeolites can act as a molecular sieve since it has the ability to adjust the pores to precisely determined uniform openings to allow only molecules smaller than its pore diameter to be adsorbed whilst excluding larger molecules (*Zeolite molecular sieve* 2008). This property can be fine tuned by varying the structure by changing the size and number of cations around the pores. Other applications can take place within the pore includes polymerisation of semiconducting materials and conducting polymers to produce materials having unusual physical and electrical attributes (*Zeolite applications* 2009a).

In ion exchange, hydrated cations within the zeolite pores are bound loosely to the zeolite framework, and can readily exchange with other cations when in aqueous media (*Zeolite applications* 2009a). Common applications of zeolites in ion exchange are applied in water softening devices, and in detergents and soaps. Also, the removal of radioactive ions from contaminated water (*Zeolite applications* 2009a).

2.7.1 ZSM-5

In this research, ZSM-5 (Zeolite Socony Mobil-5) shown in Figure 2.9 is selected as the catalyst for catalytic cracking of tar in biomass palm shells gasification process. The pore size of ZSM-5 is 5.1 to 5.6 Å (Sadeghbeigi 2000, 120). The preparation of this zeolite involves hydrothermal crystallisation, a reaction carried out in aqueous solutions at a temperature of 160ºC for a few days (*Synthesis and characterisation of the Zeolite ZSM-5*, 1995). The shape selectivity of ZSM-5 allows preferential cracking of long-chain, low octane normal paraffins, as well as some olefins, in the gasoline fraction (Sadeghbeigi 2000, 120). Prior used of ZSM-5 catalyst in experiment, calcination is required to be performed on the catalyst in the furnace at a temperature of 600°C for duration of 4 hours to convert the ZSM-5 catalyst into HZSM-5 catalyst.

In industrial, ZSM-5 is added to the unit to boost gasoline octane and to increase light olefin yields. This can be accomplished by upgrading low-octane components in the gasoline boiling range (C_7 to C_{10}) into light olefins (C_3, C_4, C_5) as well as isomerising low-octane liner olefins to high-octane branched olefins (Sadeghbeigi 2000, 121). The use of ZSM-5 is the cheapest way of octane enhancement with the additional advantage of the formation of the formation of C_3-C_5 alkenes for alkylate feed and for oxygenate formation (Olah and Molnár 2003, 37).

ZSM-5's effectiveness depends on several variables. The catalytic crackers that process highly paraffinic feedstock and have lower base octane will receive the greatest benefits of using ZSM-5 but will have little effect on improving gasoline octane in units that process naphthenic feedstock or operate at a high conversion level (Sadeghbeigi 2000, 121).

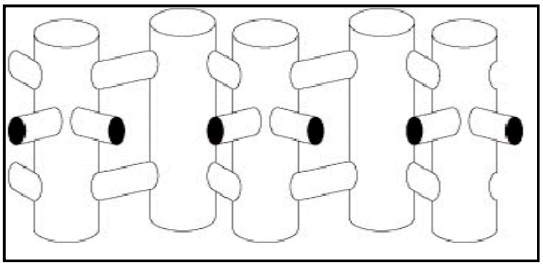


Figure 2.9: Schematic of the pore structure of ZSM-5.

2.8 CONCLUSIONS AND SPECIFIC OBJECTIVES FOR THE PRESENT STUDY

Biomass gasification had given much interest during these recent years in the replacement of the depleting amount of fossil fuels. Biomass properties are one of the key parameters of successful operation of gasification in terms of moisture, ash, alkalis and volatiles content.

The major problems associated with biomass gasification is the production of fine particulates, ashes, alkali metal compounds, nitrogenous compounds such as ammonia from the fuel bound nitrogen and higher hydrocarbons which will result in operating problems (condensation), piping, and linked to gas turbines or internal combustion engine. These contaminants need to be removed to the standard specification limits of gas turbine. Therefore, extensive gas clean up is required to meet stringent fuel quality requirements in prevention of erosion and corrosion of the downstream equipment, and environmental problems.

Catalytic cracking is chosen as the hot gas clean up in the laboratory scale gasification process in this research as it is considered to be one of the most promising methods for tar elimination and does not generate wastewater (Saxena et al. 2008, 1916).

In the current investigation, ZSM-5 catalyst is selected as a catalyst for hot gas clean up in the fixed updraft bed reactor since it has been successfully used as a catalyst for fluid catalytic cracking (FCC) units in oil refineries in oil industries to increase the motor octane of gasoline, increase the total liquefied petroleum gas (LPG) and increase the olefin content of the fraction (Sadeghbeigi 2000). The benefits of using this catalyst are its ease of availability, its low cost and prior usage as catalyst in FCC units. Since no studies have been carried out using this catalyst on gasification processes using palm shells feedstock, therefore, it will be worthwhile to study the catalytic cracking effect of this catalyst on the tar produced from biomass palm shells gasification.

In the following chapters we will

- Discuss the experimental pinch scale process for a proposed gas cleanup technologies system.
- Study the cleaning efficiency of tar removal using HZSM-5 material with respect to the variation in operating parameters such as air to nitrogen ratio, temperature, presence of catalysts and the particle sizes of biomass oil palm shells.
- Develop suitable equations from the experimental results on the prediction of tar content.

Chapter 3 Research Methodology and Techniques

3.1 BACKGROUND

Chapter 2 has outlined the present understanding of the major problems associated with biomass gasification. It has been indicated that the production of fine particulates, ashes, alkali metal compounds, nitrogenous compounds such as ammonia from the fuel bound nitrogen and higher hydrocarbons will result in operating problems, piping, and linked to gas turbines or internal combustion engine. Among all the contaminants, tar is the most problematic contaminants as it does not only caused blockages in exit pipes, clogged particulate filters and caused various impacts to the downstream processes but also the carcinogenic character of the tar could endangered the health of living things and the tar contain a significant amounts of energy that can be transferred to the fuel gas as H_2, CO, CH_4 and others (Abu et al. 2004, 6911). Therefore, the elimination of tars produced in this system is crucial, as the tolerance limit of the gas turbine on tar is less than 0.5 g/Nm^3 which if not been removed within the mentioned limit will lead to damage or an unacceptable level of maintenance of turbines (Belgiorno et al. 2003, 8).

As it has been mentioned in Chapter 2, most of the research conducted using biomass palm shells as gasification feedstock investigated on the gas composition, gas yield, and gas heating value. And also, mostly experiments are conducted in a fluidised bed gasifier from previous studies when using this feedstock. Fluidised bed had been commonly used as gasifier from previous studies due to the ability to offer higher throughput and greater fuel flexibility such as handling low-density feedstock like undensified crop residues or sawdust (Johansson, Bodlund, and Williams 1989).

Due to no studies carried out to investigate the effect of the byproducts especially tars from the gasification of biomass palm shells, therefore an experimental study on the gasification of palm shells with air-nitrogen mixtures as gasification agent in a laboratory scale atmospheric pressure updraft fixed bed reactor is carried out in this research.

Fixed bed reactor is selected over fluidised bed, as pyrolysis vapours produced from the updraft fixed bed reactor configuration allows effective internal heat exchange compared to downdraft fixed bed reactor (Belgiorno et al. 2003, 4). Besides that, the gas quality is easier to be controlled and less particulate carryover in this reactor configuration (Williams and Larson 1996, 159).

HZSM-5 catalyst is placed in situ with the biomass palm shells in the gasifier of 60 mm inner diameter and 280 mm height to determine the effectiveness of the cracking of the tar produced in this system.

Although the main concern in this research is the byproduct of tar produced from the palm shells gasification, the emissions of CO, NO, and SO_2 production and biomass gasification index (BGI) will also be presented in this research.

The main operating variables studied are nitrogen flow rate (3-7 LPM) with fixed flowrate of compressed air (5 LPM), average biomass palm shells particle size, (1.18-7.13 mm), percentage of calcined HZSM-5 catalyst (2-10%) on the effect of BGI tar content, emission of CO, NO, and SO_2 production.

This chapter outlines the research methodology, experimental approach and analytical techniques that are used to achieve these purposes. A description for each phase is presented as below:

Phase I: Samples Preparation.

Biomass palm shells are obtained from a local palm oil mill. Properties of the palm shells are determined. These palm shells are stored for use throughout this study.

Commercial HZSM-5 catalyst is used and it is calcined prior to be used in experiments.

Phase II: Experimental Apparatus.

A bench-scale fixed bed updraft gasifier system is designed and installed, and then some initial tests were conducted for commissioning before actual experimental run are conducted.

Phase III: Experimental Procedures.

A fixed amount of palm shells, 130 grams and varied amount of calcined HZSM-5 catalyst (2 to 10%) depending on the experiment run is placed together in the laboratory updraft fixed bed gasifier. Mixtures of nitrogen gas and compressed air are supplied to the reactor as the gasifying agent.

Phase IV: Experimentation and Data Analysis.

A detailed experimental programme in Section 3.5 to study the effect of biomass gasification index (BGI), tar content, emissions of CO, NO, and SO_2 on the main operating variables of average palm shells particle size, nitrogen to oxygen ratio, and weight percentage of calcined HZSM-5 catalyst used is summarised in Table 3-3.

The experimental results obtained for each response variable will be compared statistically using Minitab (v. 15) software.

Besides that, models for the tar removal cleanup for syngas derived from biomass oil palm shells is developed and verified.

Phase V: Tar analysis.

The results of gas chromatographic analysis on the tar produced in this experiment are discussed. The method involved in this analysis is outlined in this chapter.

3.2 SAMPLES PREPARATION

3.2.1 Biomass Palm Shells Feedstock

- ***Characteristics of Biomass Palm Shells***

Biomass palm shell used as biomass gasification feedstock is shown in Figure 3.1. The palm shells are obtained from Galasah palm oil mill in Miri, Sarawak. The typical proximate, ultimate and chemical element analysis of palm shells are presented in Table 3-1.

Figure 3.1: Biomass palm shells.

Table 3-1: Proximate, ultimate and chemical analysis of palm shells (Islam et al. 1999, 74 and Azali et al. 2005, 74).

Analysis Results	Weight %
Proximate Analysis	
Volatiles	68.8
Fixed Carbon	20.3
Moisture	8.4
Ash	2.3
Ultimate Analysis	
Carbon	55.35
Hydrogen	6.43
Nitrogen	0.37
Oxygen	38.01
Chemical Element Analysis	
Al	1.65
B	5.84
Ca	0.47
Cd	0.00
Cr	0.04
Fe	0.35
K	2.20
Mg	0.24
Na	2.79
P	0.07
Pb	0.01
S	0.19
Si	86.07
Ti	0.08

- ***Preparation of Biomass Palm Shells***

Sieve analysis or gradation test is conducted on the undistributed palm shells before proceeding to gasification experiment.

The purpose of sieve analysis is to assess the particle size distribution on the undistributed palm shells. Palm shells are weighed before pouring into the top sieve which has the largest screen openings (>9.50 mm). Each lower sieve in the column has smaller openings than the one above. The sieve sizes used are >9.50 mm, 4.75-9.50 mm, 2.36-4.75 mm, 1.18-2.36 mm, and <1.18 mm. All the impurities and dusts

accumulated remained into the receiver. The column is typically placed in a mechanical shaker. The shaker shakes the column for duration of 10 minutes.

After the shaking is completed the material on each sieve is weighted.

Figure 3.2 shows the palm shells particle size distribution. It is seen that size distribution of 4.75-9.50 mm had the highest weight fraction, 0.62 followed by size distribution 2.36-4.75 mm and >9.50 mm respectively. The least weight fractions of the palm shells size distribution are 1.18-2.36 mm and <1.18 mm.

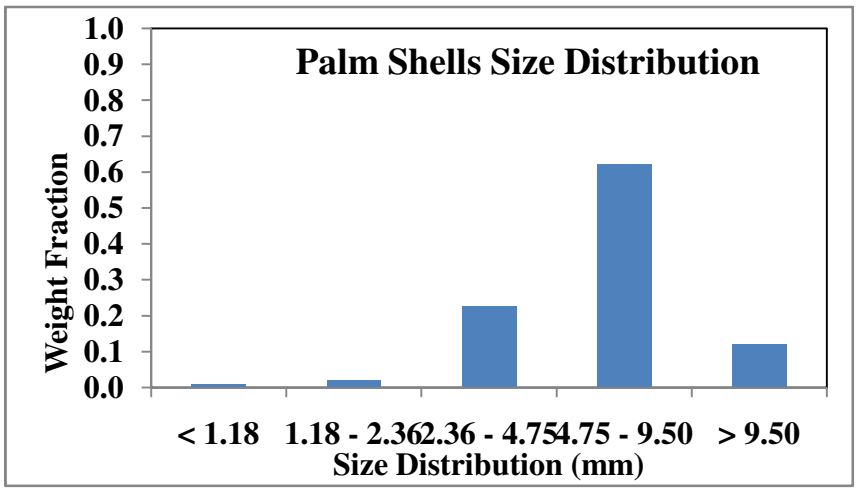


Figure 3.2: Histogram for palm shells size distribution.

3.2.2 HZSM-5 Catalyst

- ***Properties of HZSM-5 Catalyst***

HZSM-5 is commercially obtained from Zeolyst International. It contains a two dimensional 10-ring pore structure, with one set of pores in zig-zag, or sinusoidally shaped (Zeolyst International n.d.). The properties of HZSM-5 catalyst are presented in Table 3-2.

Table 3-2: Properties of HZSM-5 Catalyst (Zeolyst International n.d.).

SiO_2/Al_2O_3 ***(Mole Ratio)***	30
Nominal Cation Form	Ammonium
Na_2O ***(Weight %)***	0.05
Surface Area ***(m^2/g)***	400
Appearance	White Powder
Odour	Odourless
pH	Not applicable
Specific Gravity	>1
Solubility in Water	Negligible

- ***Preparation of HZSM-5 Catalyst***

Fresh HZSM-5 is placed in a ceramic crucible before calcination is performed in the furnace at a temperature of 600°C for duration of 4 hours. After calcination, the ceramic crucible with calcined HZSM-5 is placed in desiccator for 3 hours. The desiccator contained silica gel which acts as a desiccant or adsorbent that attracts water vapour molecules to prevent humidification of moisture adsorption in the calcined HZSM-5. Thereafter, the calcined HZSM-5 is stored in a dried container at room temperature prior use. Figure 3.3 shows the fresh and calcined HZSM-5 which does not show any much difference in appearance and colour.

Figure 3.3: Fresh (left) and calcined (right) HZSM-5 catalyst.

3.3 EXPERIMENTAL APPARATUS

The experimental set-up consists of three main parts: (i) fixed bed updraft reactor, (ii) tar collection section and (iii) gas sampling section as illustrated in Figure 3.4. Figure 3.5 shows the photo of the experimental setup. Further details on the experimental setup are described in the following section.

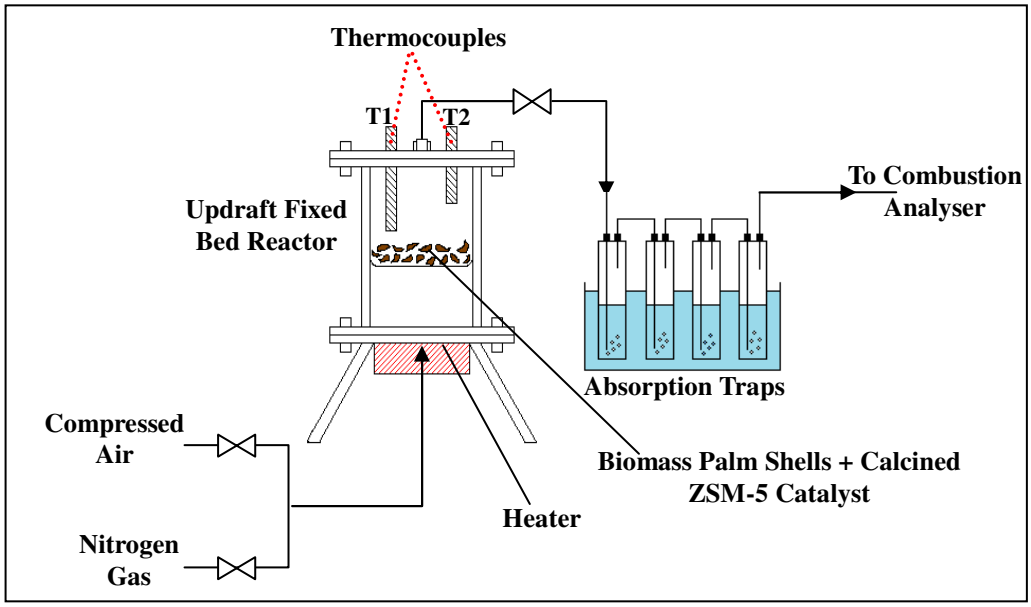


Figure 3.4: Experimental setup of laboratory fixed bed reactor system.

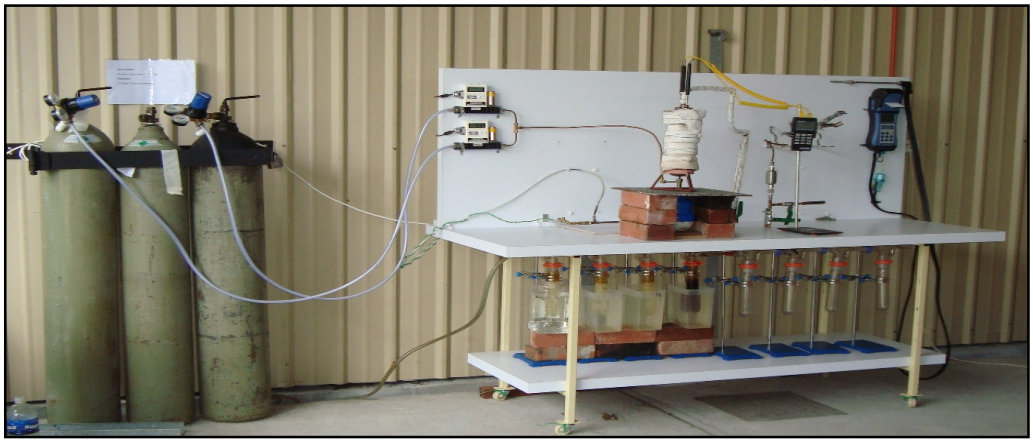


Figure 3.5: Photo of laboratory fixed bed reactor system.

3.3.1 Gasifier Unit

The fixed bed updraft reactor is made of stainless steel 304 with an inner diameter of 60 mm and a height of 280 mm. Fixed bed updraft reactor is selected as the gasifier

since the internal heat exchange is much effective compared to downdraft reactor (Beligiorno et al. 2003, 4). This can be further explained that all the tars must pass through a hot bed of char in this configuration which leads to a lower tar levels compared to updraft gasifier (*Biomass gasification* 2007). Asbestos is used to insulate the reactor to minimise heat dissipated to the surrounding.

Two K-type thermocouples (T1 and T2) are installed inside the reactor to detect temperature of the dense bed, defined as gasification reaction zone (at the height of 20 mm above the distributor) and freeboard zone (at the height of 140 mm above the distributor) respectively.

The diameter of holes in distributor diameter is 0.1 cm. All the tubing used in this experiment setup is made of ¼" diameter copper. Copper is selected as the material of construction due to its malleable and ductile physical properties and also can be able to withstand to a temperature of 1083°C (CopperInfo 2010).

Nitrogen gas and compressed air is supplied to the reactor as the gasifying agent. The flowrates of nitrogen gas and compressed air supplied to the reactor is controlled using a gas regulator in order to control the amount of oxygen to nitrogen ratio supplied to the gasifier.

Figure 3.6: Laboratory scale fixed bed updraft reactor.

3.3.2 Tar Collection Section

So far no well-developed and standardised measurement method exists for tars in biomass-producer gases, and different sampling and analysis methods are currently being used. This is because the measurement methods as well as definitions for tars are numerous and non-consistent (Energy Research Centre of the Netherlands (ECN) n.d.).

The method developed by Hasler and Nussbaumer (2000) is used for tar sampling in this research. This method allows longer duration sampling for the determination gas contaminants in the range of 3 hours if necessary and also it is applicable to atmospheric fixed bed gasifiers.

The tar collection section consists of four condenser or absorption traps (250 mL each), containing approximately 200 mL of distilled water. Condenser traps are washed with water and rinsed using acetone prior the use. The four condenser traps are immersed in water at room temperature. During sampling, tars are condensed and trapped in the water and formed two insoluble layer liquids. The tar will sink in the bottom of the condenser traps as the tar is denser than water. The mixture is separated using Advantec filter paper (125 mm diameter, 6 μm particle retention) and evaporated under room temperature for at least 3 hours to remove any remaining water. The weight of the tar produced is measured in order to calculate the concentration of the tar.

Tar concentration, C_t is generally defined as the total weight of tars per unit volume of syngas as shown in Equation (3.1).

$$C_t = \frac{W_t}{V_s} \tag{3.1}$$

where

C_t = Concentration of tars in syngas (mg/Nm^3)
W_t = Weight of tars in syngas (mg)
V_g = Normal volume of syngas (Nm^3)

Figure 3.7: Absorption traps for tar collection.

3.3.3 Gas Sampling Section

The main sampling point for the gas analysis is located at the gas outlet point as it passes through the stainless steel probe of the combustion analyser, Euroton UniGas 3000+ Mk3. The combustion analyser is used to measure CO, NO, and SO_2 in terms of parts-per-million (ppm). The temperature of the sampling measured is at 33°C.

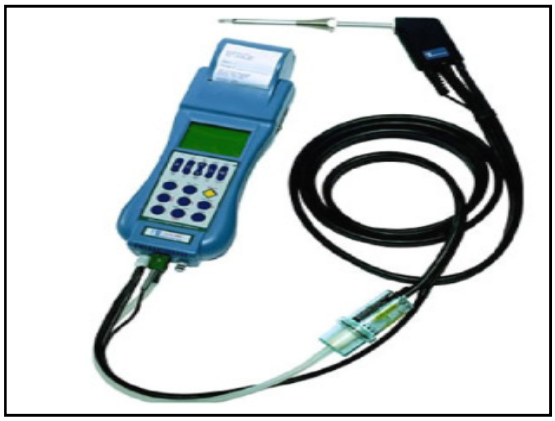


Figure 3.8: Combustion analyser (Eurotron UniGas 3000+ Mk3).

3.4 EXPERIMENTAL PROCEDURES

At the start-up of each experimental run, the palm shells and calcined HZSM-5 are charged into the reactor. The quantity of palm shells used for each experimental run is 130 grams. The quantity of calcined HZSM-5 placed in the reactor in situ with the palm shells is depending on the experimental run. The reactor is then heated up to a temperature approximately 250°C at which the volatiles of the palm shells started to

be released, and temperature then grows fast. Thereafter, the mixture of the compressed air to nitrogen gas is set and supplied into the reactor.

The gas leaving the heated reactor is cooled in a series of four absorption traps, where most of the tars are collected.

Experiment is terminated when the temperature decreased to a temperature approximately 500°C. The HZSM-5 catalyst and palm shells are sieved. Thereafter, the remainder weight of the palm shells is measured after the experiments are performed in order to calculate Biomass Gasification Index (BGI).

BGI is defined as the ratio of the biomass weight differences to the initial weight of the biomass used in the process as in Equation (3.2). Each experiment is repeated 3 times for each set.

$$BGI = \frac{W_i - W_f}{W_i} \times 100\% \tag{3.2}$$

where W_i = Initial weight of palm shells before experiment (g)

W_f = Final weight of palm shells after experiment (g)

3.5 EXPERIMENTATION

The detailed experimental programme is as summarised in Table 3-3 to study the effect of biomass gasification index (BGI), tar content, emissions of CO, NO, and SO_2 on the main operating variables of average palm shells particle size, nitrogen to oxygen ratio, and weight percentage of calcined HZSM-5 catalyst used.

Table 3-3: A summary of experimental programme for fixed bed updraft reactor in this study.

Palm Shells		***HZSM-5 Catalyst***	***Nitrogen Flowrate***	***Compressed Air***
Size Fractions (mm)	**Average Size Particle, d_p (mm)**	**Weight %**	**Litres per Minute (LPM)**	
2.36 - 4.75	3.56	0	5	5
4.75 – 9.50	7.13		7	
< 2.36	1.18		3	
2.36 - 4.75	3.56		5	
4.75 – 9.50	7.13		7	
< 2.36	1.18		3	
2.36 - 4.75	3.56		5	
4.75 – 9.50	7.13		7	
< 2.36	1.18	2	3	
2.36 - 4.75	3.56		5	
4.75 – 9.50	7.13		7	
< 2.36	1.18		3	
2.36 - 4.75	3.56		5	
4.75 – 9.50	7.13		7	
< 2.36	1.18		3	
2.36 - 4.75	3.56		5	
4.75 – 9.50	7.13		7	
< 2.36	1.18	5	3	5
2.36 - 4.75	3.56		5	
4.75 – 9.50	7.13		7	
< 2.36	1.18		3	
2.36 - 4.75	3.56		5	
4.75 – 9.50	7.13		7	
< 2.36	1.18		3	
2.36 - 4.75	3.56		5	
4.75 – 9.50	7.13		7	
< 2.36	1.18	10	3	
2.36 - 4.75	3.56		5	
4.75 – 9.50	7.13		7	
< 2.36	1.18		3	
2.36 - 4.75	3.56		5	
4.75 – 9.50	7.13		7	

The experimental results obtained for each response variable will be compared statistically using Minitab (v. 15) software.

In the first stage of using this software, the standardised Pareto's diagram is used to observe the estimated effects of the independent variables and their possible interactions on the dependent variables. A Pareto chart is a special type of bar chart where the values plotted are arranged in descending order (Kutner et al. 2004). Analysis of variance (ANOVA) is then used to study the influence of the independent variables (average palm shells particle size, nitrogen to oxygen ratio, and weight percentage of calcined HZSM-5 catalyst used) and their possible interactions on the dependent variables (BGI, tar content, emissions of CO, NO, and SO_2). The observed variance is partitioned into components due to different explanatory variables (Aznar et al. 2008). The basis of the comparison of the variance caused by the variation of each studied factor (nitrogen to air ratio, average palm shells particle size, and percentage of calcined HZSM-5 catalyst) are the variance caused by experimental error, which is calculated from the replicated of center points for each response variable. In order to consider that one factor has a statistically significant influence on a response variable, the variance caused by the factor is divided by the error variance, and the F-test is used with a 95% confidence level.

3.6 ANALYTICAL TECHNIQUE FOR TAR ANALYSIS

Gas chromatographic technique was used to analyse the chemical composition in volume % in the collected tar samples. The detailed procedures required in gas chromatographic analysis are based on method developed by Simell et al. (2000, 35-36) as mentioned in the following section.

3.6.1 Gas Chromatographic Analysis

Gas chromatographic analysis is carried out on the tar samples to measure the chemical composition of the tar as the tar composition is strongly dependent on the operating conditions of the gasification process.

Equipment: Gas chromatograph (HP 5890), and Integrator (HP 3396A).

Column: HP Ultra 2 or equivalent (Crosslinked 5% Ph Me silicone) length 50 m, diameter 0.32 mm, film thickness 0.52 μm.

Detector: FID (temperature 310°C).

Injector: Split/splitless injector, temperature 280°C.

Carrier gas: Helium, injector pressure about 120kPa, total flow about 20 ml/minute.

Oven: Start 50°C, initial holding time 5 minutes, heating rate 3.0°C/minutes to 160°C, then heating rate 10.0°C/min to 290°C, holding time 150 minutes.

Injection: Autosampler 1μl, split injection, sample in dichloromethane.

Solvent: Dichloromethane (minimum purity 99%)

Tar Components: Dodecane ISTD, Benzene, Pyridine, Toluene, *m*-Xylene, Ethynylbenzene, Styrene, *O*-Xylene, Phenol, 4-Methylstyrene, Indene, Napthalene, Quinoline, Isoquinoline, 2-Methylnaphtalene, 1-Methylnaphthalene, Biphenyl, 2-Ethylnaphthale, Acenahthylene, Acenaphthene, Dibenzofurane, Fluorene, Phenantrene, Anthracene, 4*H*-Cyclopenta[def]phenanthrene, Fluoranthene, and Pyrene.

3.7 CONCLUSION

In this chapter, the samples preparation, experimental apparatus, experimental procedures, experimentation, and analytical technique for tar analysis had been discussed.

Before the samples preparation could be conducted, the biomass palm shells are obtained from Galasah palm oil mill in Miri, Sarawak and the HZSM-5 catalyst are obtained commercially from Zeolyst International. The undistributed palm shells undergoes sieve analysis or gradation test to assess the particle size distribution on the undistributed palms shells. The biomass palm shells are then stored in a dried place based on their particle size distribution. As for the HZSM-5 catalyst preparation, fresh HZSM-5 catalyst had to be calcined in a temperature of 600°C for duration of 4 hours.

Thereafter, the calcined HZSM-5 catalyst are placed in a dessicator containing silica gel for the prevention of humidification of moisture adsorption in the calcined HZSM-5 prior storing in a dried container at room temperature.

The experimental setup consists of three main parts namely fixed bed updraft reactor, tar collection section and gas sampling section. The fixed bed updraft reactor is made of stainless steel 304 with an inner diameter of 60 mm and a height of 280 mm. This type of reactor is selected as the internal heat exchange is much effective compared to downdraft reactor (Belgiorno et al. 2003, 4). The method developed by Hasler and Nussbaumer (2000) is used for tar sampling in this research as this method allows longer duration sampling for the determination gas contaminants in the range of 3 hours if necessary and also applicable to atmospheric fixed bed gasifier. The tar collection section consists of four condenser of absorption traps (250 mL each), containing approximately 200 mL of distilled water. For the gas sampling section, the main sampling point for the gas analysis is located at the gas outlet point as it passes through the stainless steel probe of the combustion analyser, Eurotron UniGas 3000+ Mk3 to detect gas emission gases such as CO, NO, and SO_2.

The research methodology has been developed to suit the system. A fixed amount of biomass palm shells weighed 130 grams and varied amount of calcined HZSM- 5 catalyst from 2 to 10 weight % are placed together in the laboratory updraft fixed bed gasifier depending on the experiment run. The mixtures of nitrogen gas and compressed air are supplied to the reactor as the gasifying agent.

A detailed experimental programmed had been summarised to study the effect of biomass gasification (BGI), tar content, emissions of CO, NO, and SO_2 on the main operating variables of average palm shells particle size, nitrogen to oxygen ratio, and weight percentage of calcined HZSM-5 catalyst used.

Experimental results obtained will then be compared statistically using Minitab (v.

15) software. Thereafter, analysis of variance (ANOVA) is then used to study the influence of the independent variables (average palm shells particle size, nitrogen to oxygen ratio, and weight percentage of calcined HZSM-5 catalyst used) and their possible interactions on the dependent variables (BGI, tar content, emissions of CO, NO, and SO_2). And also, suitable equations are developed and verified for the tar removal cleanup for syngas derived from biomass oil palm shells.

Tar samples collected will undergo gas chromatographic analysis based on method developed by Simell et al. (2000, 35).

Chapter 4 Results and Discussion

In this chapter, studies are carried out on,

(i) results of gas chromatography analysis on the biomass palm shells tar produced,

(ii) influences of nitrogen flowrate and particle size on the biomass gasification index (BGI), tar content, emissions of CO, NO, and SO_2, and percentage of HZSM-5 catalysts ,

(iii) suitable equations for the tar removal cleanup for syngas derived from biomass oil palm shells.

4.1 GAS CHROMATOGRAPHY ANALYSIS ON TAR

4.1.1 Effect of Different Oxygen to Nitrogen Ratio

The results were obtained from ITS Testing Services (Malaysia) Sdn Bhd for tar analysis using gas chromatographic equipment.

The methods used and the list of chemical components mentioned by Simell et al. (2000, 36) are used as a basis to develop a task for gas chromatographic analysis to detect the chemical components in the tar produced in this system.

The chemical components detected in each sample by the gas chromatographic is stated and quantified in volume percentage. The results are presented in histogram as shown in Figure 4.1 to 4.3. It is found that the chemical components detected from the gas chromatographic analysis of the tar consists of aromatics and polyaromatics hydrocarbon in the tar.

The varying amount of nitrogen flowrate supplied to the gasifier is to control the oxygen to nitrogen ratio fed into the gasifier.

In Figure 4.1, the histogram shows the chemical components detected in three different tar samples obtained from different oxygen to nitrogen ratio supplied to the gasifier.

All the chemical components indicated in Figure 4.1 belong to the tar group. Carbolic acid, o-methoxy phenol, 2-methoxy-p-cresol, diethyl phthalate, o-cresol, p-ethylguiacol, o-guaiacol, and 2-methoxy-p-cresol are classified under heterocyclic aromatics meanwhile 1, 3-dimethoxy-2-hydroxybenzene is classified under light aromatic (1 ring) class.

It is observed from Figure 4.1 that the tar contains a high concentration of carbolic acid approximately 5 to 8 volume% of the gas with the varying flowrate of oxygen to nitrogen ratio flowrate. The carbolic acid concentration increases when the decrease of the oxygen to nitrogen ratio supplies.

For oxygen to nitrogen ratio of 0.10, the chemical components appeared in the tar are carbolic acid, o-cresol, p-ethylguiacol, o-guaiacol, and 2-methoxy-p- cresol.

For oxygen to nitrogen ratio of 0.12, the chemical components appeared in the tar are carbolic acid, diethyl phthalate, 1, 3-dimethoxy-2-hydroxybenzene, o-cresol, and p-ethylguiacol.

For oxygen to nitrogen ratio of 0.15, the chemical component appeared in the tar are carbolic acid, o-methoxy phenol, 2-methoxy-p-cresol, diethyl phthalate, and 1,3-dimethoxy-2-hydroxybenzene.

Since majority of the tar components are classified under the heterocyclic aromatics except for 1, 3-dimethoxy-2-hydroxybenzene, these chemical components exhibit high water solubility (Devi 2005, 36) and these tars are normally formed at a temperature 700°C (Stevens 2001). The high solubility of the heterocyclic tar is due to

its high polarity. The disadvantage of this tar is that they may lead to hazardous wastewater, resulting in high disposal or processing cost for low temperature gas cleaning systems (Paasen and Kiel 2004, 12). And also, lead to a considerable increase in tar dewpoint aggravating tar condensation and aerosol formation (Paasen and Kiel 2004, 3). It is highly recommended to find alternative to eliminate these tars rather than disposing it as waste liquid stream. Therefore, in section 4.1.2, the presence of HZSM-5 catalyst in the experiment is to determine whether heterocyclic aromatics in the tar can be easily destroyed.

It is observed that the overall heterocyclic aromatics in the tar content are comparable when operating with oxygen to nitrogen ratio of 0.12 and 0.15.

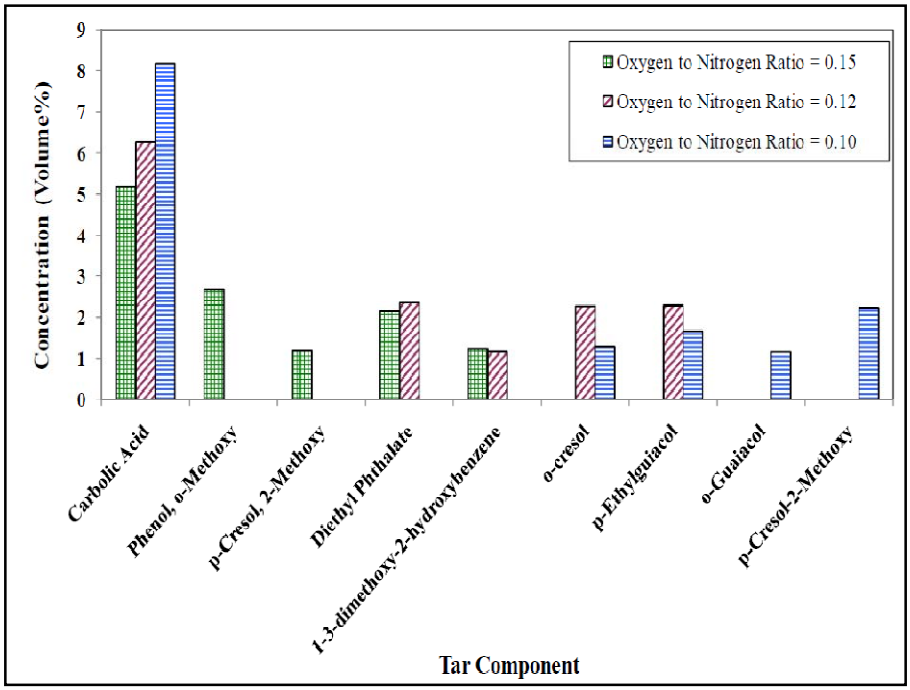


Figure 4.1: The chemical components detected through gas chromatography analysis in the tar produced when operating with different oxygen to nitrogen ratio without presence of catalyst.

4.1.2 Effect of Different Percentage of HZSM-5 Catalyst

Figure 4.2 and 4.3 illustrate the chemical components found in the tar produced when operating at oxygen to nitrogen ratio of 0.15 and 0.10 respectively with the presence of catalyst in different percentage.

It is observed from Figure 4.2 that with the presence of HZSM-5 catalyst, the concentration of carbolic acid is significantly reduced. The lowest concentration of carbolic acid can be obtained when using 5 weight % of HZSM-5 catalyst which is up to 79 weight % reduction when compared without the presence of HZSM-5 catalyst used. This clearly shows that HZSM-5 catalyst can effectively reduced the heterocyclic compounds in tar. Since this chemical component of the tar could lead to hazardous wastewater, HZSM-5 catalyst used for catalytic cracking could benefit in destroying tar rather than transforming them to a waste liquid stream that is very difficult to dispose (Corella, Toledo, and Padilla 2004, 2433). Besides that, this method does not required as high temperature compared to thermal cracking and could save operating cost of this system.

It is also observed from Figure 4.2, as the percentage of the catalyst increased, less chemical compounds are found in the tar which means that most of the chemical components in the tar had been eliminated. When no catalyst is used, the chemical compounds found in the tar are carbolic acid, o-methoxy phenol, 2-methoxy p-cresol, and diethyl phthalate.

With 2 weight % catalyst, only carbolic acid and 2-metoxylpyridine are detected in the tar. As for 5 and 10 weight % of catalyst used, only carbolic acid appeared in the tar content.

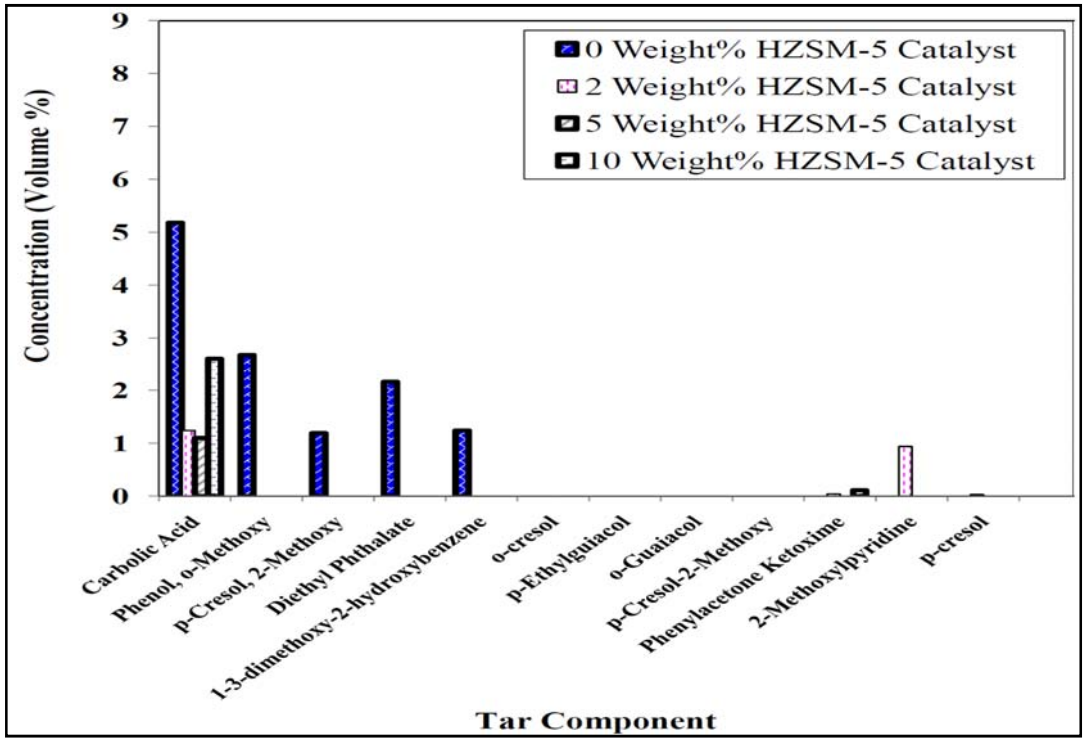


Figure 4.2: The chemical components detected through gas chromatography analysis in the tar produced when operating at oxygen to nitrogen ratio of 0.15 with the presence of HZSM-5 catalyst.

From Figure 4.3, it is observed that carbolic acid still presence in the tar when tested in the range of different percentage of catalyst and at reduce rate of oxygen to nitrogen of 0.10. It is also seen that carbolic acid appeared to have the highest concentration without the presence of catalyst and significantly reduced with the presence of catalyst. The least amount of concentration of carbolic acid can be achieved approximately 0.05 volume % of the gas when 5 weight % catalysts is used at this nitrogen flowrate. The least amount of chemical component appeared in the tar when 5 and 10 weight % of catalyst are used in experiments. In the presence of 2 weight % catalyst, the chemical components exist in the tar are carbolic acid, diethyl phthalate, and o-guaiacol. For 5 and 10 weight % catalyst, only carbolic acid appeared in the tar.

Overall, HZSM-5 catalyst can be recommended to be used in this system. It has significantly reduced the carbolic acid in tar when the percentage of the catalyst is increased from 2 to 10 weight %. Besides that, this catalyst had significantly reduced

most of the chemical components found in the tar produced without the presence of catalyst.

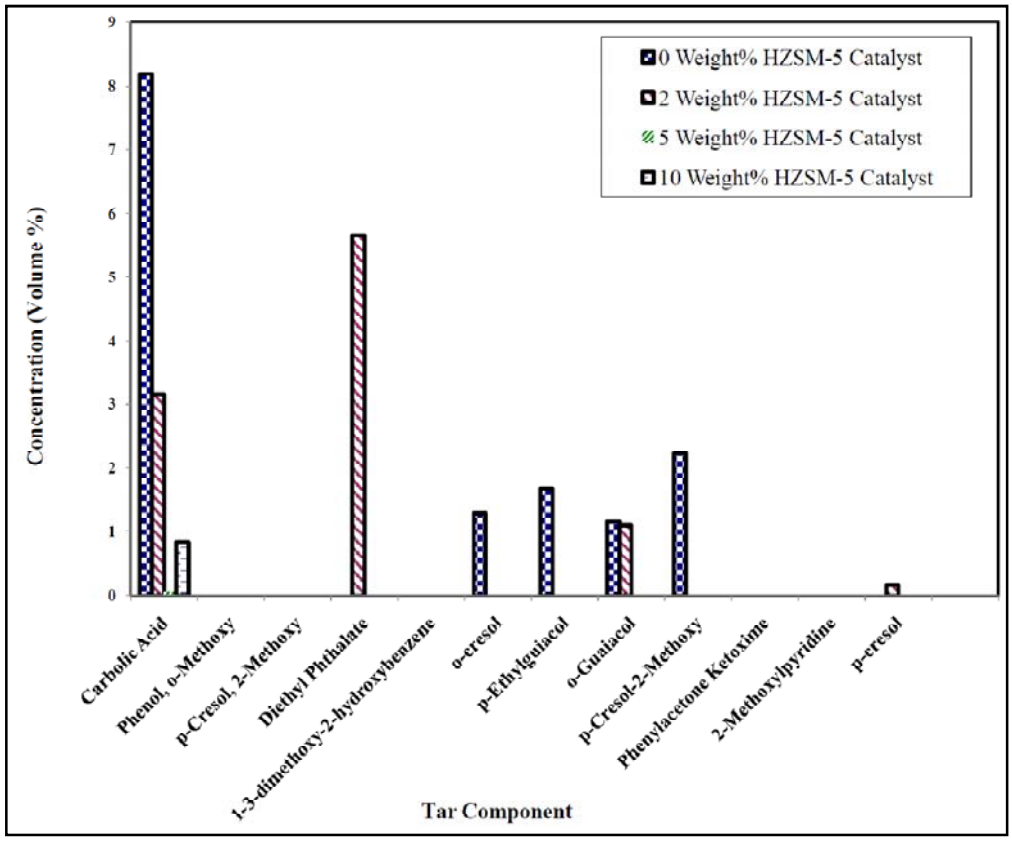


Figure 4.3: The chemical components detected through gas chromatography analysis in the tar produced when operating at oxygen to nitrogen ratio of 0.10 with the presence of HZSM-5 catalyst.

4.2 INFLUENCES OF NITROGEN FLOWRATE AND PARTICLE SIZE ON THE BIOMASS GASIFICATION INDEX (BGI), TAR CONTENT, EMISSIONS OF CO, NO AND SO_2 AND PERCENTAGE OF HZSM-5 CATALYSTS

In this section, Pareto plot is selected from Minitab (v. 15) software to detect the factor and interaction effects which are important in this study. The independent variables involved in this study are average palm shells particle size, nitrogen flow rate, and weight percentage of calcined HZSM-5 catalyst used. The correspond dependent variables are the biomass gasification index (BGI), tar content, emissions of CO, NO, and SO_2. The Pareto's chart displays the absolute values of the effects and draws a reference line on the chart. Minitab displays the absolute value of the standardised

effects of factors when there is an error term (Antony 2003, 36). As for the reference line displayed in the Pareto's chart, if any effects that extend beyond the reference line is said to be significant at the default level of alpha = 0.05.

It is realised to be more convenient to represent nitrogen and air flowrate in terms of LPM rather than oxygen to nitrogen ratio when using Pareto's chart.

4.2.1 Influence of Nitrogen Flowrate and Particle Size on Biomass Gasification Index (BGI)

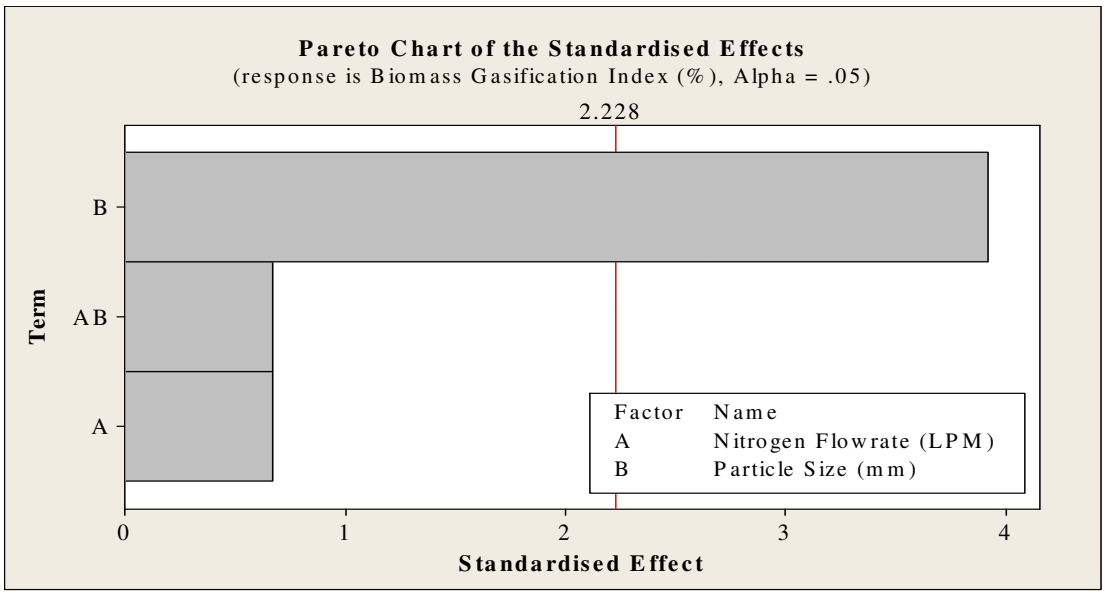
It is observed from Figure 4.4 that the palm shells particle size has a significant effect on the BGI in the range of variable studied.

Figure 4.5 shows the interaction plot on the effect of different palm shells particle size on its BGI. Using palm shells particle size between 1.18 to 7.13 mm, the BGI varied between 80 % and 89 % when nitrogen flow rate varies from 3 to 7 LPM with constant air flow rate of 5 LPM is supplied. It is seen from Figure 4.5 that in order to obtain higher BGI, a bigger palm shells particle size are the most suitable to be used in this system.

It is view from experiments that especially palm shells particle size, 1.18 mm tends to agglomerate in the reactor compared to the two other bigger palm shells particle sizes of 3.56 mm and 7.13 mm. As a result of agglomeration, the surface area of the particle size decreases and heating rate slow down and the BGI is lowered compared to the two other particle sizes. In another words, bigger palm shells particle size are easier to be burnt compared to smaller palm shells.

Liu et al. (2009, 6505) mentioned that one of the main reasons bed agglomeration occurred is due to the condensation of alkali species in the biomass ash on the particle surfaces. The alkali metals content of the biomass and it quantities play a significant role in determining the physical properties of the material such as softening, melting points, or vaporisation points (Stevens 2001). Other than agglomeration, these alkali

compounds are also capable of enhancing hot corrosion on metallic surfaces in the process system and cementing deposited particulates (Hallgren n.d.). Several alternatives have been proposed in the literatures which may effectively reduce the agglomeration tendency, for example using alternative bed material, co-firing of the biomass with other fuel, pretreatment of fuels, and reducing bed temperature (Lahijani and Zainal 2010). Alkali compounds exceeding the gas turbine requirements (<1 ppm) will result in high temperature corrosion of turbine blades, and stripping off their protective oxide layer.



*AB represents Nitrogen Flowrate (LPM) and Particle Size (mm)

Figure 4.4: Pareto's standardised chart: Effect of the nitrogen flow rate and particle size of palm shells on BGI.

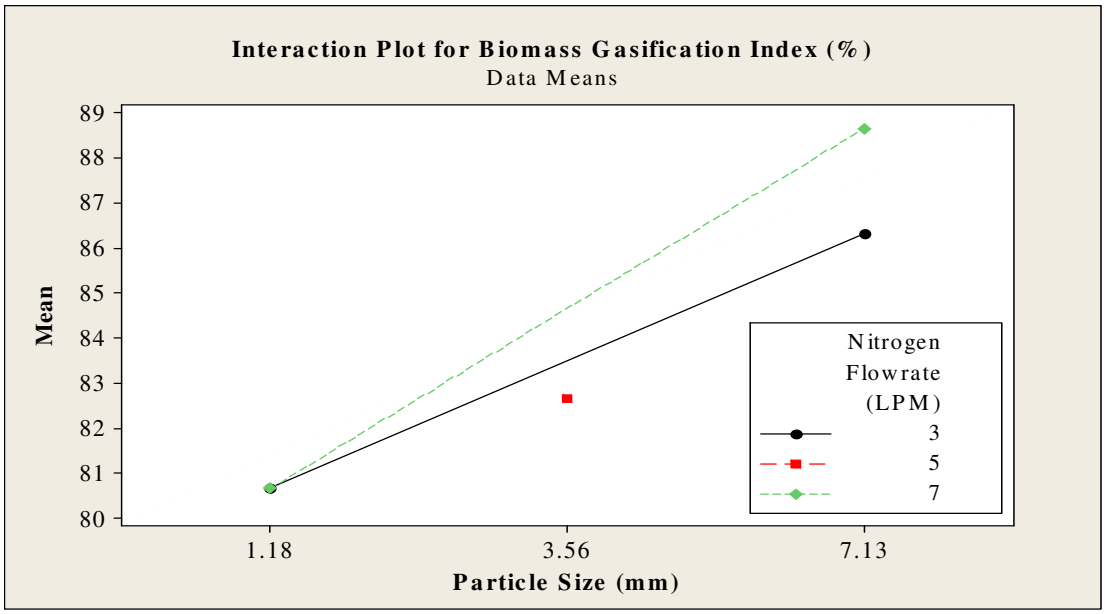


Figure 4.5: Interaction plot for BGI on the effect of the nitrogen flow rate and palm shells particle size.

4.2.2 Influence of Nitrogen Flowrate and Particle Size on Tar Content

Figure 4.6 shows that nitrogen flow rate and palm shells particle size have significant effects on the tar content.

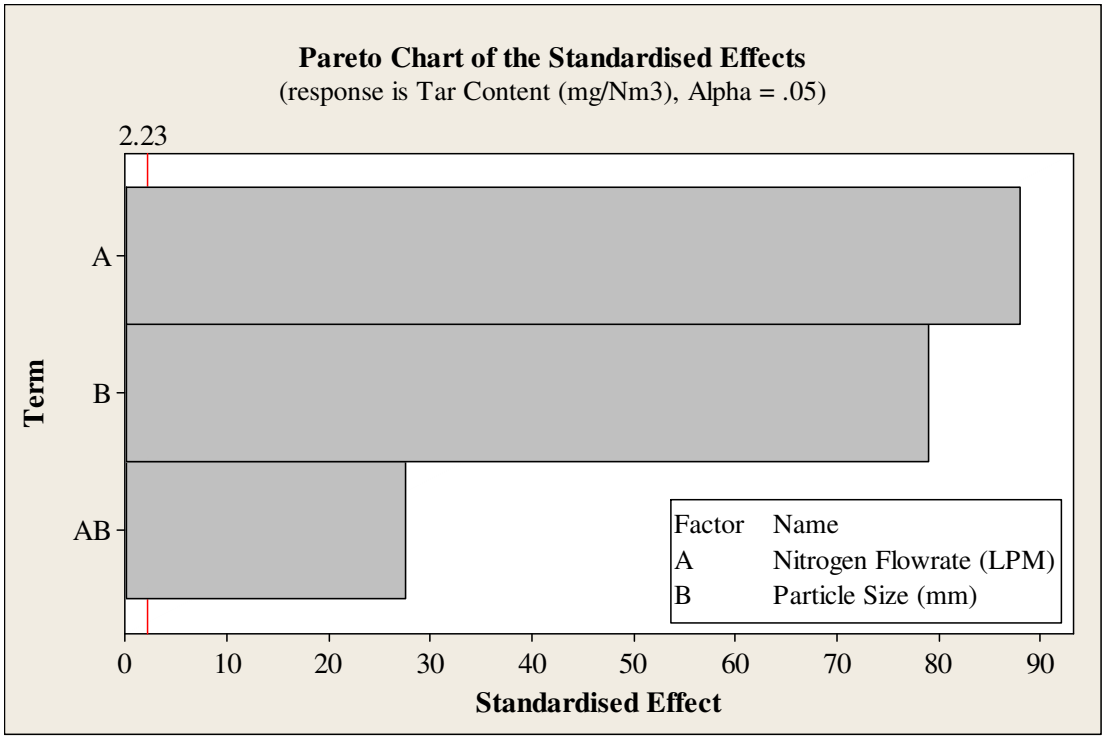


Figure 4.6: Pareto's standardised chart: Effect of the nitrogen flow rate and particle size of palm shells on tar content.

It is observed from Figure 4.7 that tar content will increase if nitrogen flow rate is increased or bigger palm shells particle size are used. When using palm shells particle size 1.18 mm, the tar content increased up to 10 times when nitrogen flowrate increased from 3 to 7 LPM. However, when a bigger palm shells particle size of 7.13 mm is used, the tar content increased up to 3 times when nitrogen flowrate increased from 3 to 7 LPM.

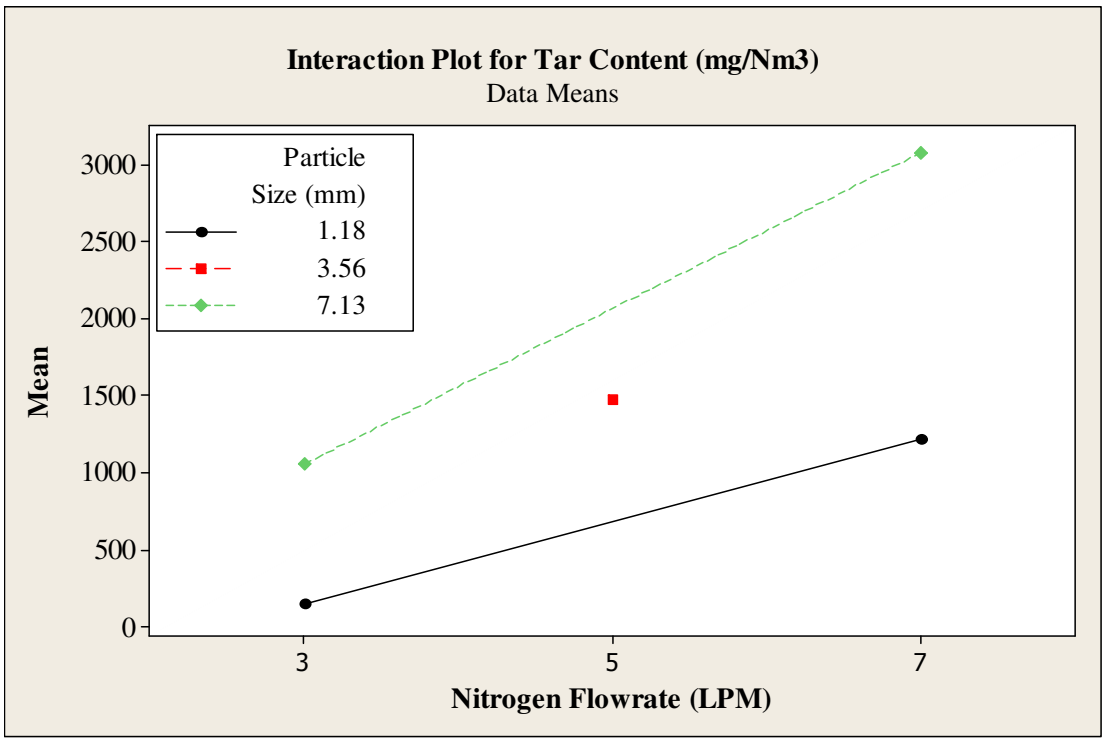


Figure 4.7: Interaction plot for tar content on the effect of the nitrogen flow rate and palm shells particle size.

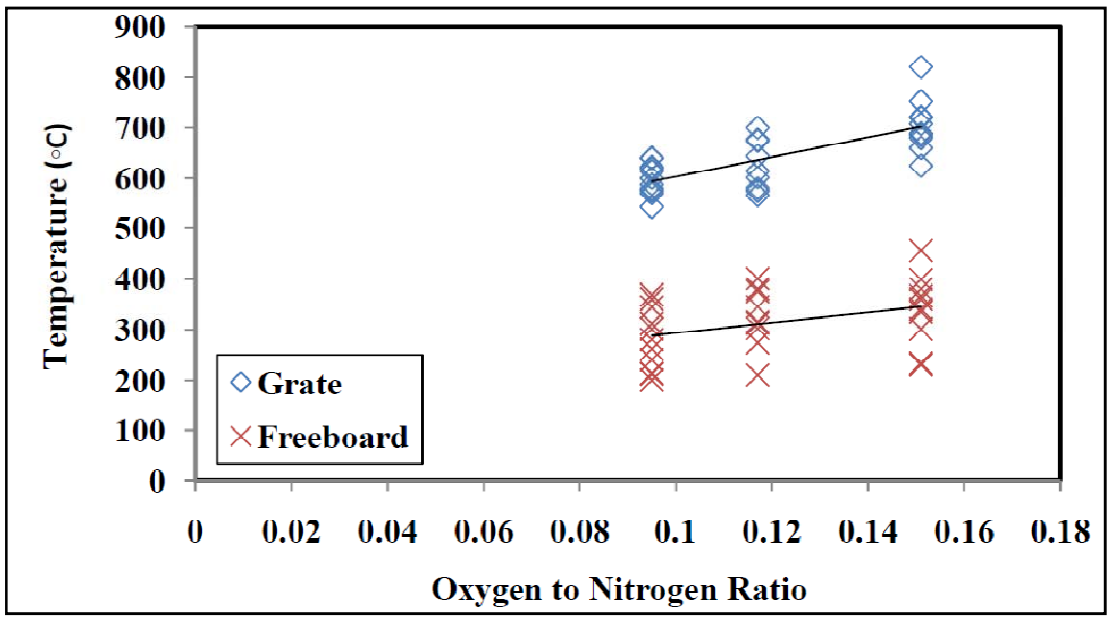


Figure 4.8: Effects of grate and freeboard temperature on different oxygen to nitrogen ratio.

Table 4-1: Oxygen and nitrogen content in the respective mixture of nitrogen and compressed air supplied to the reactor per minute.

Mixture of Gas Supplied (LPM)		**Chemical Composition (volume %)**		**Oxygen to Nitrogen Ratio**
Nitrogen	***Air***	***Oxygen***	***Nitrogen***	
3	5	13.1	86.9	0.15
5	5	10.5	89.5	0.12
7	5	8.8	91.2	0.10

Figure 4.8 show that oxygen to nitrogen ratio has more effects on the grate temperature. As the ratio of oxygen to nitrogen ratio increased, the temperature will increase as the relative oxygen concentration is increased during the pyrolysis process. The oxygen concentration is presented in Table 4-1 in the range of nitrogen flowrate studied by assuming the air composition consists of 78 volume % of nitrogen and 21 volume % of oxygen (*Air composition* 2005).

In Figure 4.7, it is observed that when nitrogen flowrate increased, the tar content will increased. This is further explained when the nitrogen flowrate is increased, the

oxygen concentration is decreased which will influence the decrease in temperature. As the result, a lower temperature is produced in the process which will lead to increase tar content.

Our measurement on the effect of the temperature on the tar concentration are in good agreement with published data on gasification (Kurkela and Ståhlberg 1992, 2, Evans et al. 1986, and Elliot 1988) and could be explained by the fact that higher temperature could improve the cracking reactions of the tar in the reactors (Aznar et al. 2008). Increasing reaction temperature will result in conversion of oxygenated tar compound to light hydrocarbons, aromatics, oxygenates and subsequently, olefins would end up as higher hydrocarbons and larger PAHs (Milne et al. 1998, 4).

Different tar compounds will give different impacts on the performance of downstream process. For examples, higher molecular mass tar compounds are easier to condense; hence this contributes to the fouling in gas cooling or gas cleaning equipment. On the other hand, oxygenated or heterocyclic tar compounds containing O and/or N atoms, for example phenol are highly soluble due to high polarity, thus may result in hazardous wastewater after the gas cleaning (Safitri 2005, 32).

Among the three palm shells particle size tested, it is observed that particle size of 1.18 mm produce the least tar amount compared to the two other particle sizes. Small particles produce heavier tar compounds, while larger particle size produces lighter PAH. This may be due to the fact that smaller particle suffers reaction in the upper side of the bed, where the atmosphere is more reduced (Padban et al. 2000). In this case, the diffusion of the volatiles from smaller particles is faster and the cracking process becomes less severe than in the case of particles with bigger size.

4.2.3 Influence of Nitrogen Flowrate and Particle Size on CO Production

As it is illustrated in Figure 4.9, the nitrogen flow rate has the most significant effects on the CO production compared to palm shells particle size. It is observed that lower nitrogen flow rate increases the CO production. As mentioned earlier, lower nitrogen flow rate will increase the temperature of the system. This is in agreement with Boudouard reaction as shown in Equation (4.1) which is an endothermic reaction. As the temperature increases, the CO production increases. This is in accordance with Le Chaterlier's principle which states that temperature favours the reactants in exothermic reactions and meanwhile endothermic reactions favour the products.

Boudouard Reaction:

$$C + CO_2 \rightarrow 2CO \qquad (\Delta H = +172\,MJ/kmol) \qquad (4.1)$$

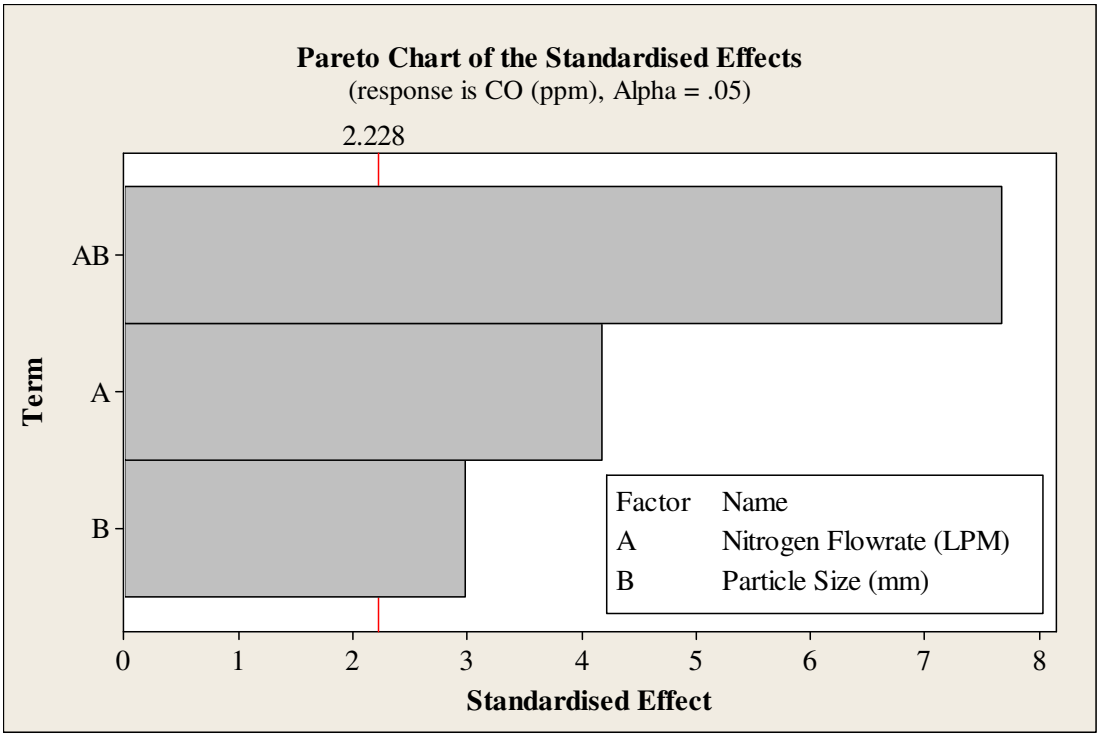


Figure 4.9: Pareto's standardised chart: Effect of the nitrogen flow rate and particle size of palm shells on CO production.

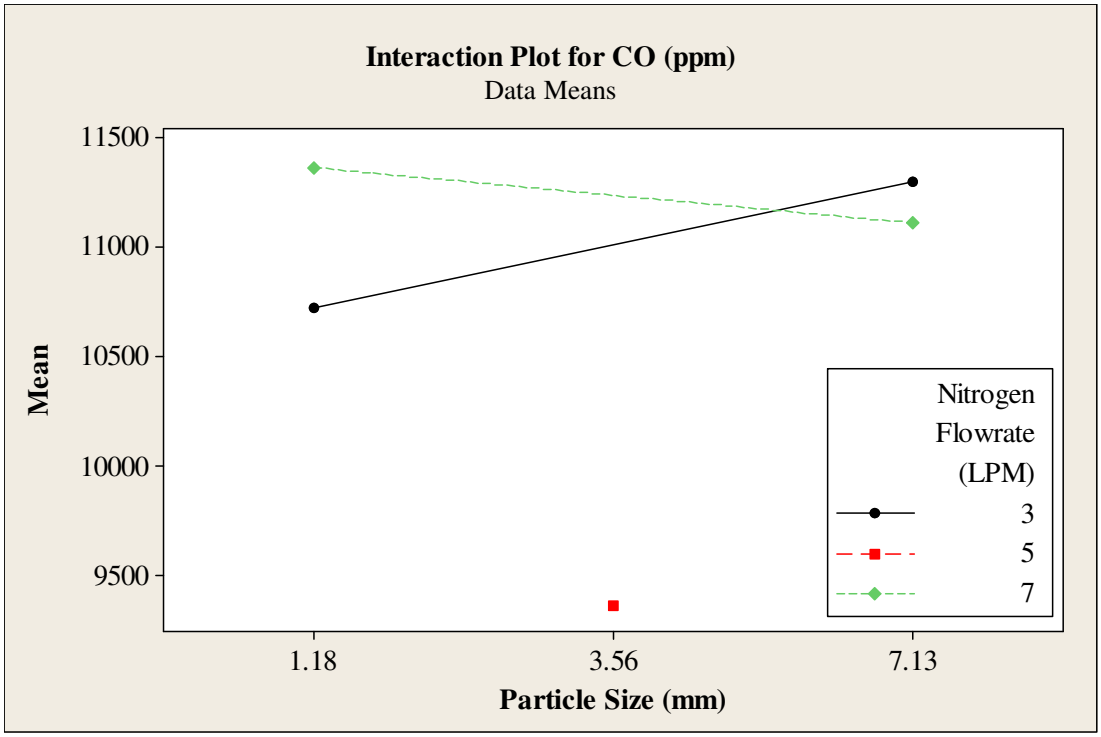


Figure 4.10: Interaction plot for CO production on the effect of the nitrogen flow rate and palm shells particle size.

4.2.4 Influence of Nitrogen Flow rate and Particle Size on NO Production

Figure 4.11 show that nitrogen flow rate has the most significant effects on the NO production compared to palm shells particle size. Generally, if the nitrogen flow rate increases, the content of NO production increases too. And also, part of the fuel nitrogen is released from the palm shells during the devolatilisation stage (Mäkinen et al. 1995, and Leppälahti and Koljonen 1995). Since the palm shells had low nitrogen content (~ 0.37 weight %), the fuel nitrogen released from the feedstock at this stage will be minimal which will not affect much on the NO production. However, as it is observed from Figure 4.12, NO production is increased when nitrogen flow rate of 7 LPM been supplied with increasing palm shells particle size. At lower nitrogen flow rate of 3 and 5 LPM, the NO production maintains almost constant regardless of the palm shells particle size.

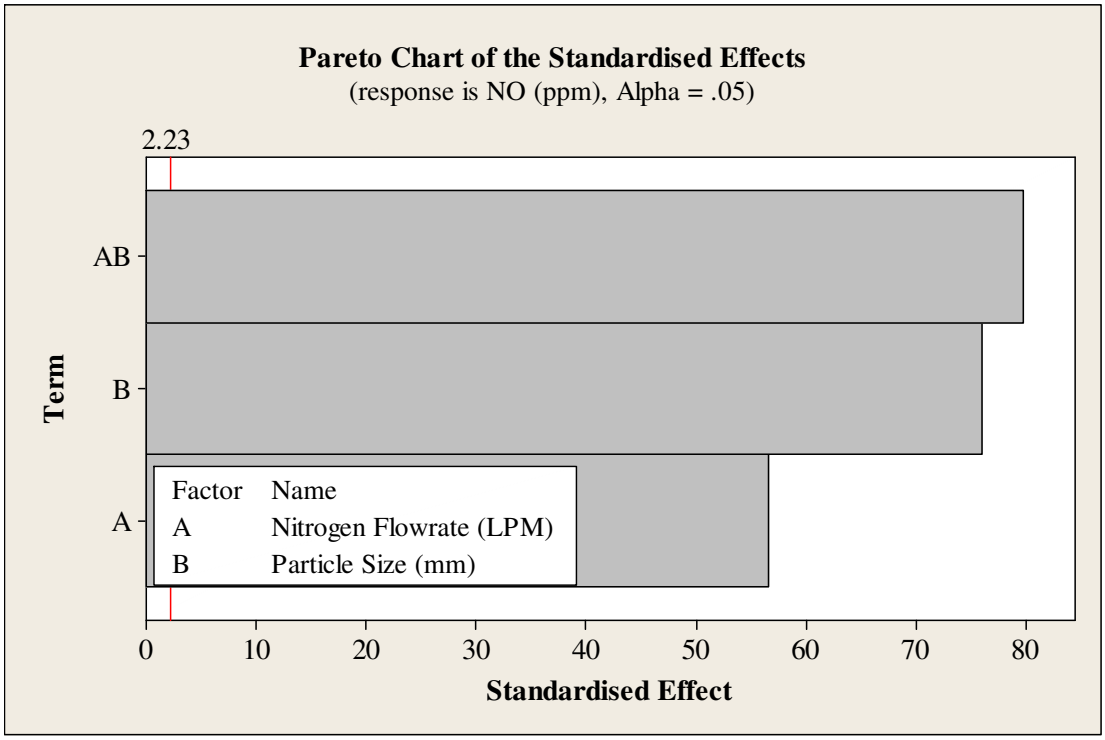


Figure 4.11: Pareto's standardised chart: Effect of the nitrogen flow rate and particle size of palm shells on NO production.

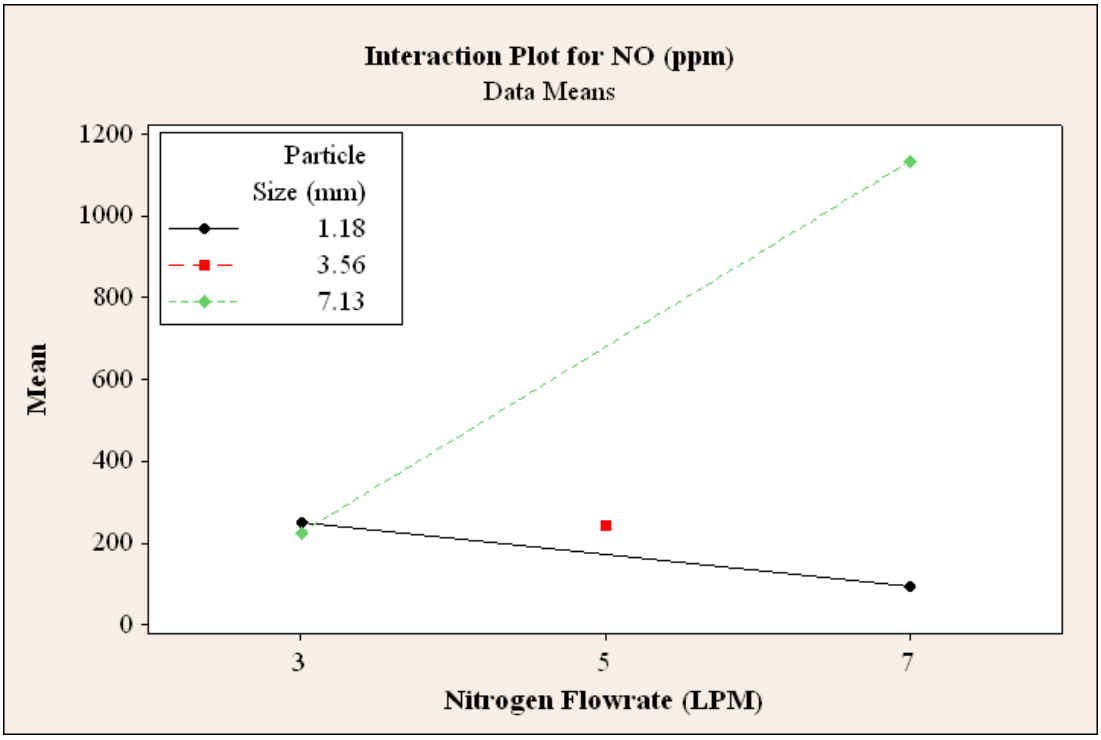


Figure 4.12: Interaction plot for NO production on the effect of the nitrogen flow rate and palm shells particle size.

4.2.5 Influence of Nitrogen Flowrate and Particle Size on SO_2 Production

Figures 4.13 and 4.14 shows that different nitrogen flow rate and palm shells particle size does not have any significant effects on the SO_2 production. According to Bridgwater (1995, 642), sulphur is not generally considered to be a problem, since biomass feeds have very low sulphur contents.

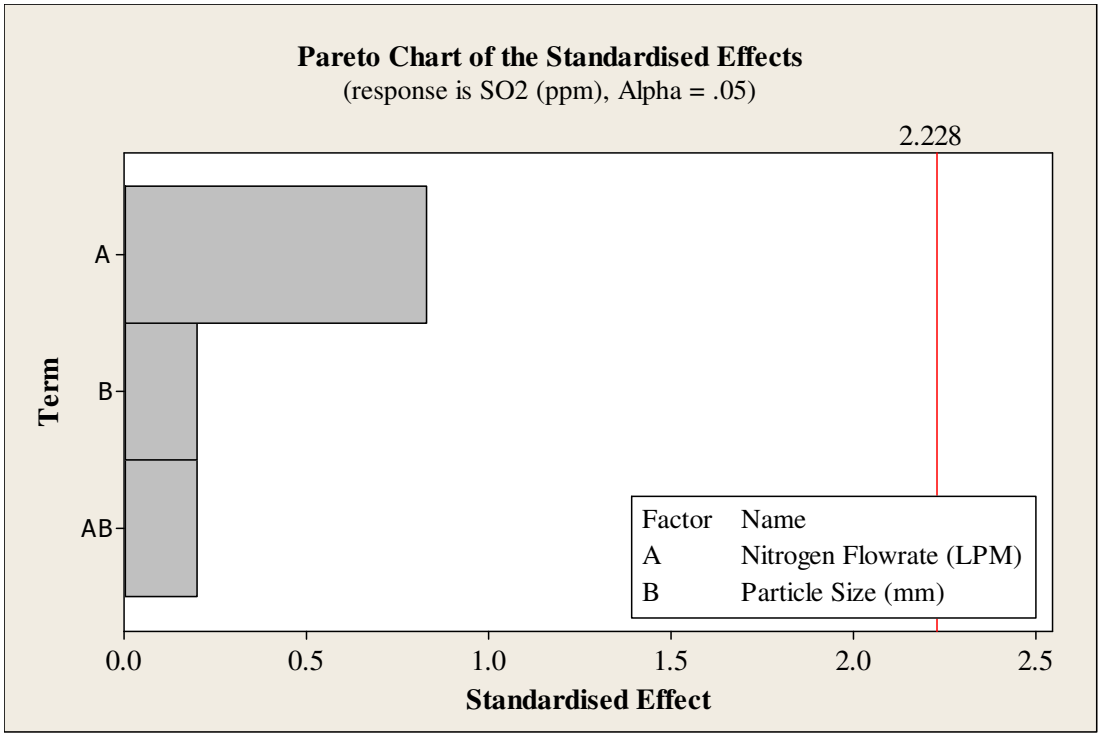


Figure 4.13: Pareto's standardised chart: Effect of the nitrogen flow rate and particle size of palm shells on SO_2 production.

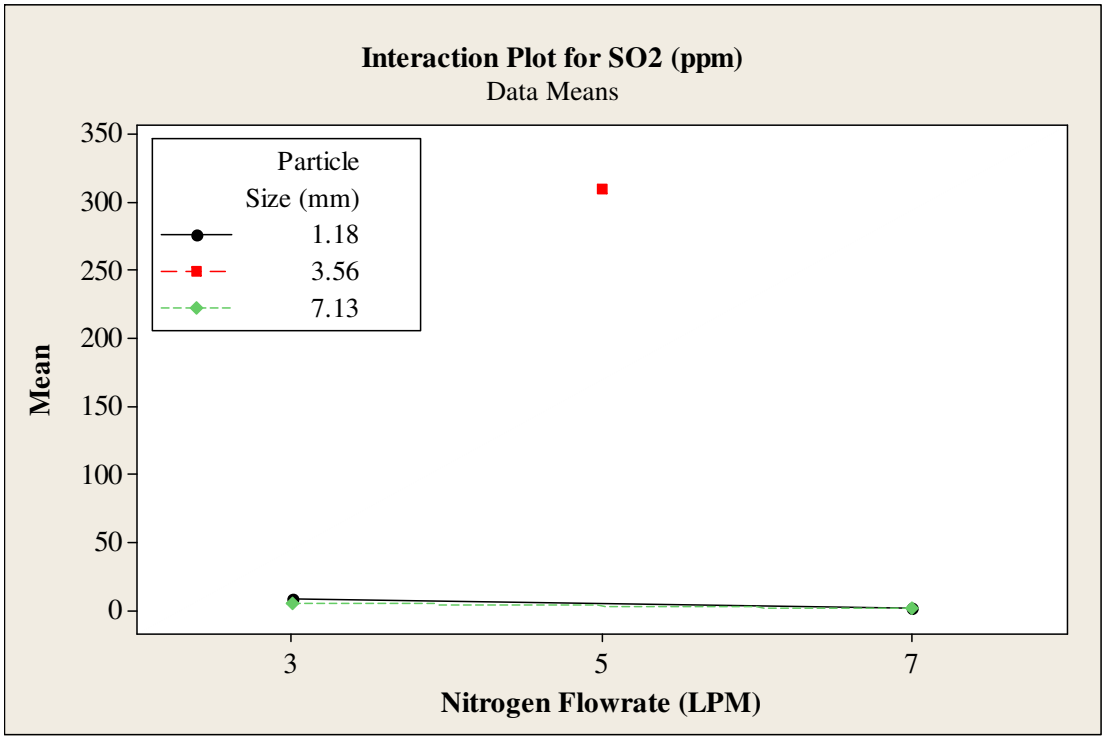


Figure 4.14: Interaction plot for SO_2 production on the effect of the nitrogen flow rate and palm shells particle size.

4.2.6 Influence of Nitrogen Flowrate, Particle Size and Percentage of HZSM-5 Catalyst on Tar Production

In Figure 4.15, the palm shells particle size and percentage of HZSM-5 catalyst placed together in situ in the reactor with the palm shells have the most significant effects on the tar content.

It is observed in Figure 4.16 that the tar content reduced up to 3 and 2.7 times for palm shells particle size 1.18 mm and 7.13 respectively in increasing percentage of HZSM-5 catalyst from 2 to 10 weight %. Among the tested percentage of HZSM-5 catalyst used, the lowest tar content can be achieved when using 10 weight % catalysts for the three palm shells particle size. It is not necessary to further reduce the tar content produced from palm shells particle size 7.13 mm when using 10 weight % catalysts as the tar content is below the gas turbine requirement, 420 mg/Nm^3. However, for the palm shells particle size of 7.13 mm when using similar percentage of catalyst, the tar content still exceeds the gas turbine requirement (<0.1 to 0.5 g/Nm^3), therefore further increase of catalyst should be tested on the tar production.

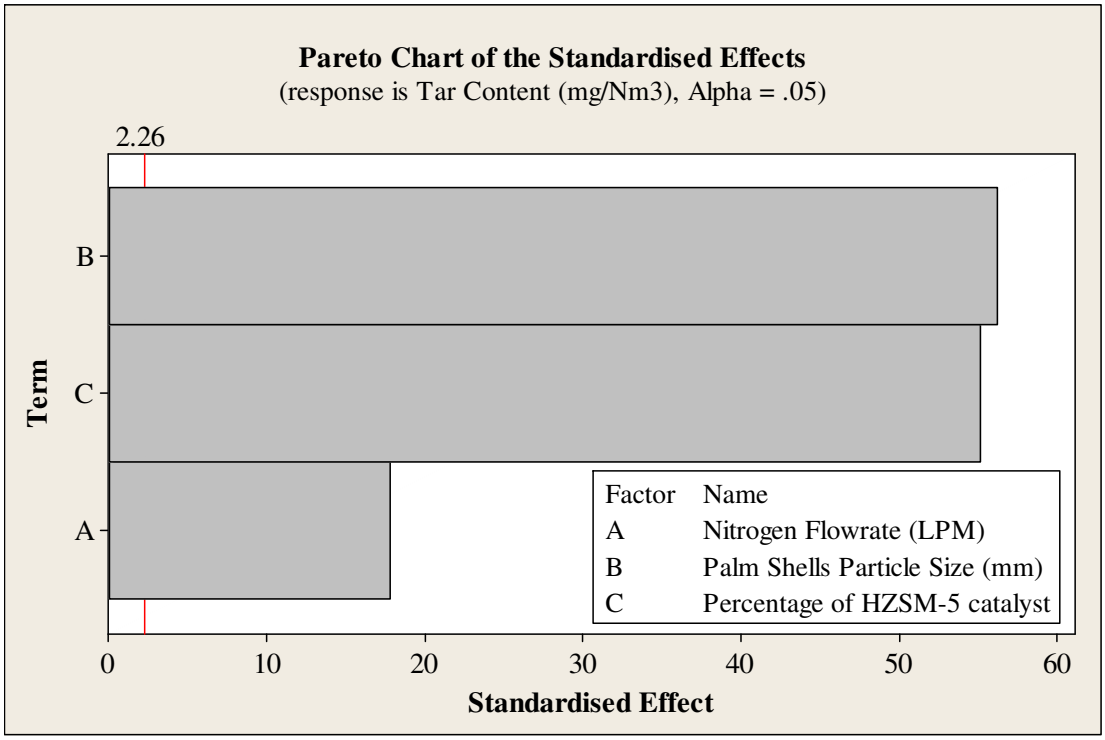


Figure 4.15: Pareto's standardised chart: Effect of the nitrogen flow rate, particle size and percentage of HZSM-5 catalyst on tar production.

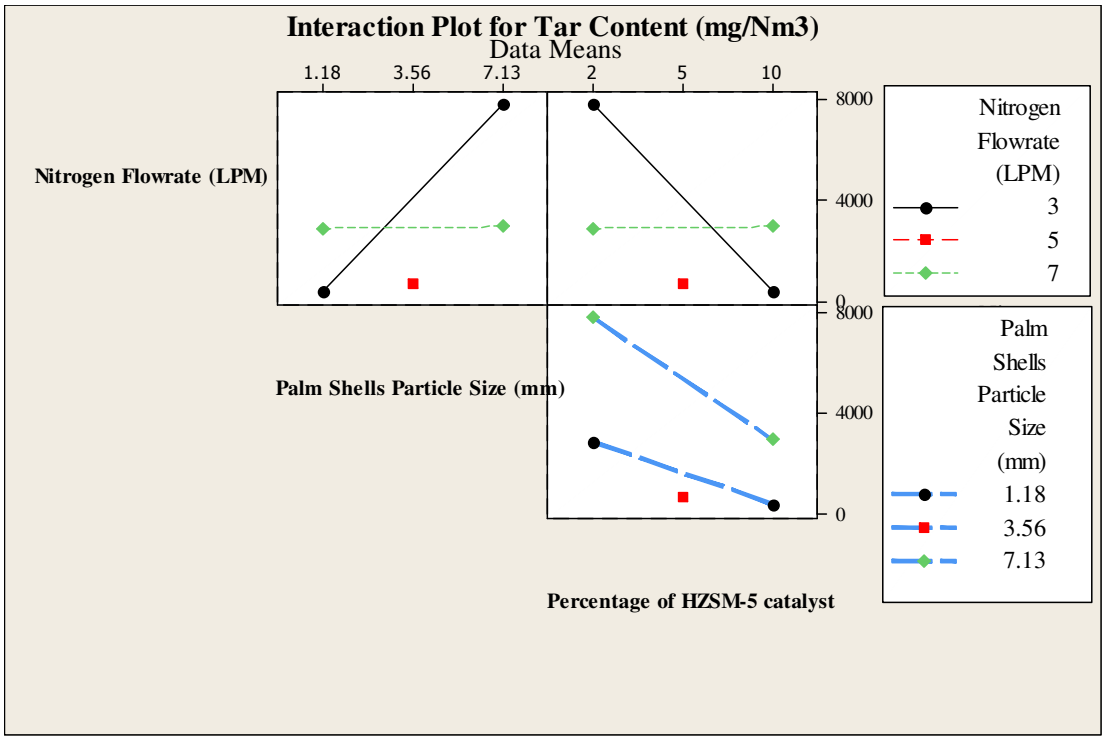


Figure 4.16: Interaction plot for tar production on the effect of the nitrogen flow rate, palm shells particle size and the percentage of HZSM-5 catalyst.

4.3 SUITABLE EQUATIONS FOR THE TAR REMOVAL CLEANUP FOR SYNGAS DERIVED FROM BIOMASS OIL PALM SHELLS

In this paragraph, the experimental data collected are utilised to develop a suitable equations for the tar removal cleanup for syngas derived from biomass oil palm shells. From the equations, the gas quality can be predicted in different operating parameters and verification can be made by comparing with experimental results from the gas cleanup process.

4.3.1 Effect of Catalyst Percentage

The effect of different percentage of zeolite HZSM-5 catalyst used in the fixed bed gasifier on the tar content at 3, 5, and 7 LPM are shown in Figures 4.17 to 4.19 respectively. It is observed overall that all the trends show a reduction effect.

The exponential lines in each figure show the predicted tar content with respect to different palm shells particle size and operating nitrogen flowrate supplied to the reactor. In Figure 4.17, the three palm shells particle sizes of 1.18, 3.56, and 7.13 mm in 3 LPM of nitrogen flow rate shows a strong decreasing effect on the tar content as catalyst increased from 2 to 5 weight % and subsequently shows a weak decreasing effect until 10 weight % of catalyst. The tar contents decreases exponentially from 2874 to 1236 (2.3 times), from 4883 to 1985 (2.5 times), and from 11122 to 4011 mg/Nm^3 (2.8 times) for palm shells particle size of 1.18, 3.56, and 7.13 mm respectively as catalyst load increased from 2 to 5 weight % in 3 LPM of nitrogen flow rate. The tar content continuously is reduced to a range of 597 to 488 mg/Nm^3 in these three palm shells particle sizes as the percentage of catalyst is increased to 10 weight %.

Figure 4.17 and Figure 4.18 show reduction trends for all three palm shells particle sizes when nitrogen flowrates of 3 LPM and 5 LPM are supplied to the reactor respectively. However, lower tar content is produced at 5 LPM of nitrogen flowrate (Figure 4.18) compared with 3 LPM of nitrogen flowrate (Figure 4.17) in the range of percentage of catalyst and palm shells particle size used. It is observed a strong

reduction in the tar content from 2 to 5 weight % of catalyst and a weak reduction in the tar content as catalyst load increased to 10 weight %. The tar content reduced significantly up to 4 times as catalyst load increased from 2 to 5 weight % and meanwhile the tar content reduced up to 2 times as catalyst increased from 5 to 10 weight % for all three palm shells particle sizes. It is observed too that there is no need to increase catalyst load greater than 10 weight % in the system as most of the tar is eliminated and the gas is considered clean as the tar content is very much below the tolerance level (tar content >500 mg/Nm^3) in the gas turbine requirement (Belgiorno et al. 2003, 8). This clearly shows that the gasification temperature is much heavily dependent on the tar content instead of the percentage of catalyst used.

However, Figure 4.19 shows an almost linear effect for all palms shells particle size when a catalyst load increased from 2 to 10 weight % in 7 LPM for this system. Further increased of catalyst load (>10 weight %) can be considered when operating at this nitrogen flowrate since the tar content is between 2834 to 881 mg/Nm^3 for all palm shells particle size when 10 weight % of catalyst is load into the gasifier. The tar content in the gas is considered high and the gas quality is still regarded as low or still "unclean" since the tar content exceeds the gas quality requirement for gas turbines.

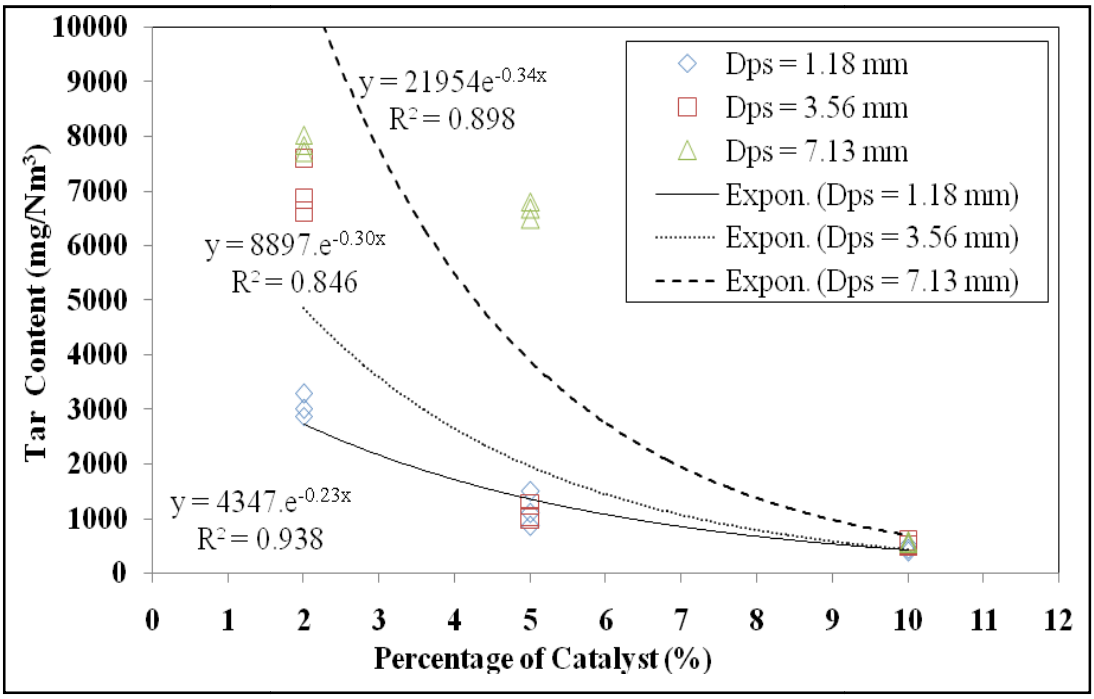


Figure 4.17: Tar content versus percentage of catalyst at 3 LPM.

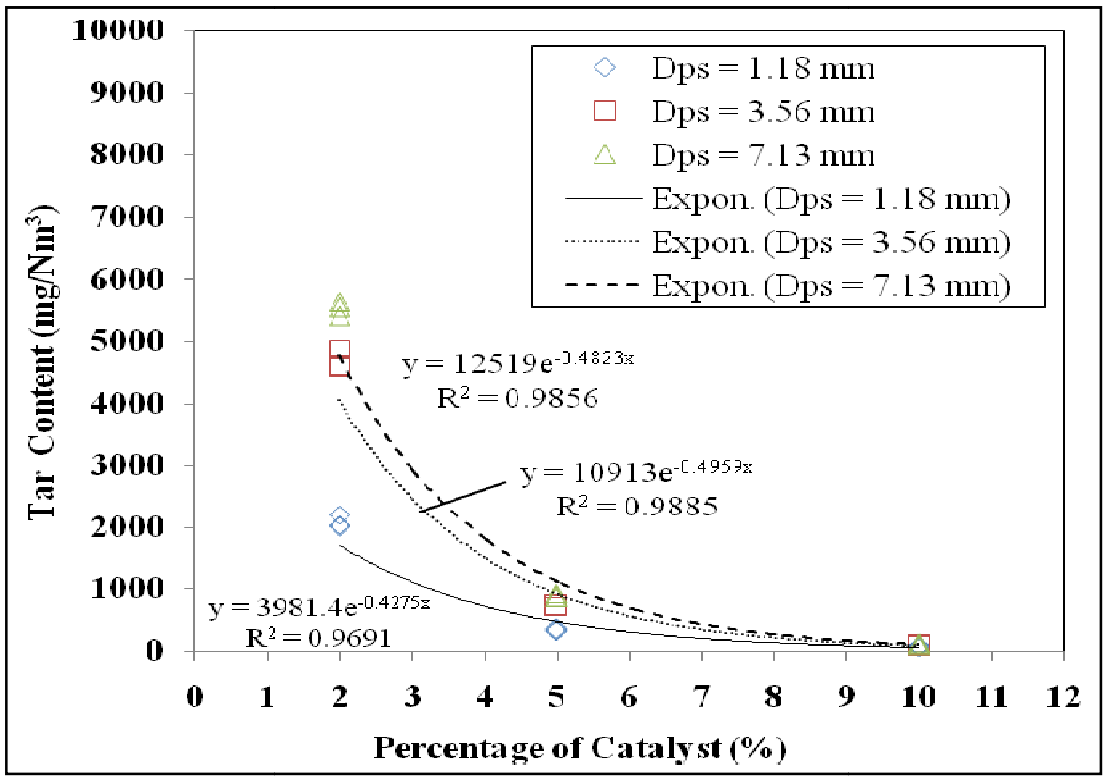


Figure 4.18: Tar content versus percentage of catalyst at 5 LPM.

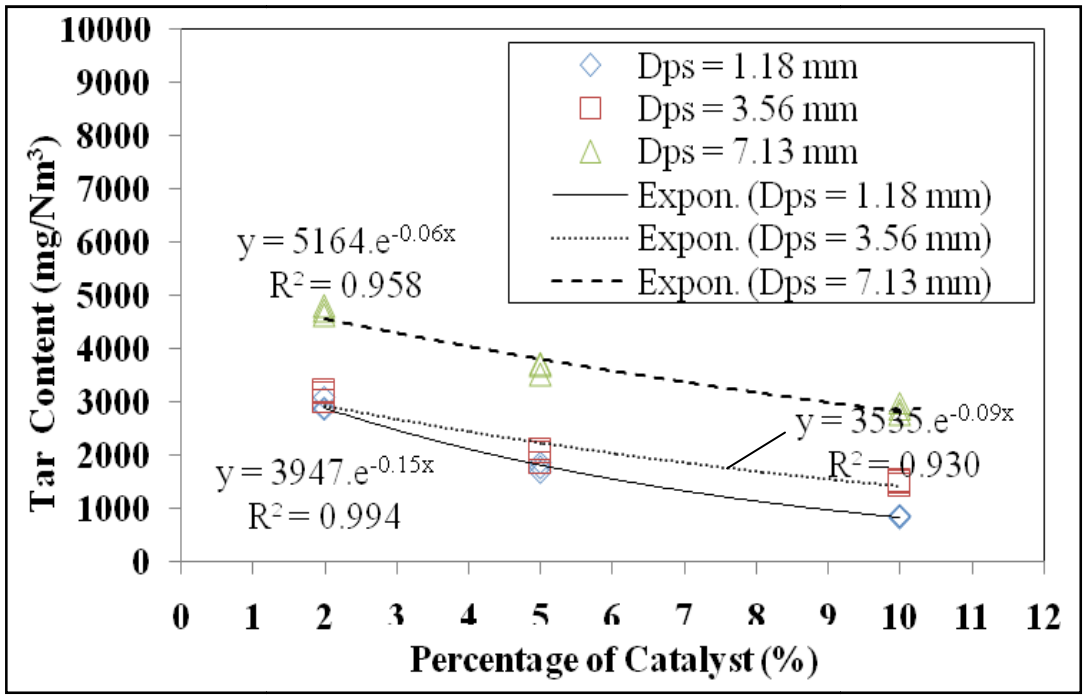


Figure 4.19: Tar content versus percentage of catalyst at 7 LPM.

4.3.2 Effect of Palm Shells Particle Size

Figure 4.20 to Figure 4.22 shows the effect of the different particle size of biomass palm shells used with respect to the tar content in the syngas. For 2 weight % catalyst, both figures 4.20 and 4.21 shows an fast increasing trend in the tar content as the palm shells increased from 1.18 to 7.13 mm. The tar content increased from 3640 to 8782 mg/Nm^3 and from 2448 to 6157 mg/Nm^3 as palm shells particle size increased from 1.18 to 7.13 mm for 3 and 5 LPM respectively in 2 weight % catalyst. However, as for 5 weight % catalyst, the tar content shows a fast increasing trend for 3 LPM and a slow increasing trend for 5 LPM as palm shells particle size increased from 1.18 to 7.13mm. The tar content increased from 851 to 5009 mg/Nm^3 and from 2448 to 6157 mg/Nm^3 as palm shells particle size increased from 1.18 to 7.13 mm for 3 and 5 LPM respectively in 5 weight % catalyst.

As for 10 weight % catalyst in both Figure 4.20 and 4.21, there are not much changes in the tar content regardless of different palm shells particle size used.

In Figure 4.22, the tar content shows a moderate of increase trend as palm shells

particle size increases from 1.18 to 7.13 mm. It is observed that the tar content will be higher as the catalyst load is decreased on the same palm shells particle size used. The tar content increases from 2811 to 4552 (1.6 times), from 1672 to 3496 (2.1 times), and from 879 to 2924 mg/Nm^3 (3.3 times) as palm shells particle size increased from 1.18 to 7.13 mm for 2, 5, 10 weight % catalyst respectively.

As observed overall, 10 weight % of zeolite catalyst gives the smallest amount of tar contents when compared with 2 and 5 weight % of zeolite catalyst used in the range of palm shells particle and the nitrogen flowrates supplied to the gasifier in this study. Figures 4.20 and 4.21 does not show any trend in tar content as palm shells particle size increases from 1.18 to 7.13 mm whereas a moderate increasing trend is seen in Figure 7.22 when 7 LPM of nitrogen flowrate is supplied for 10 weight % zeolite catalyst.

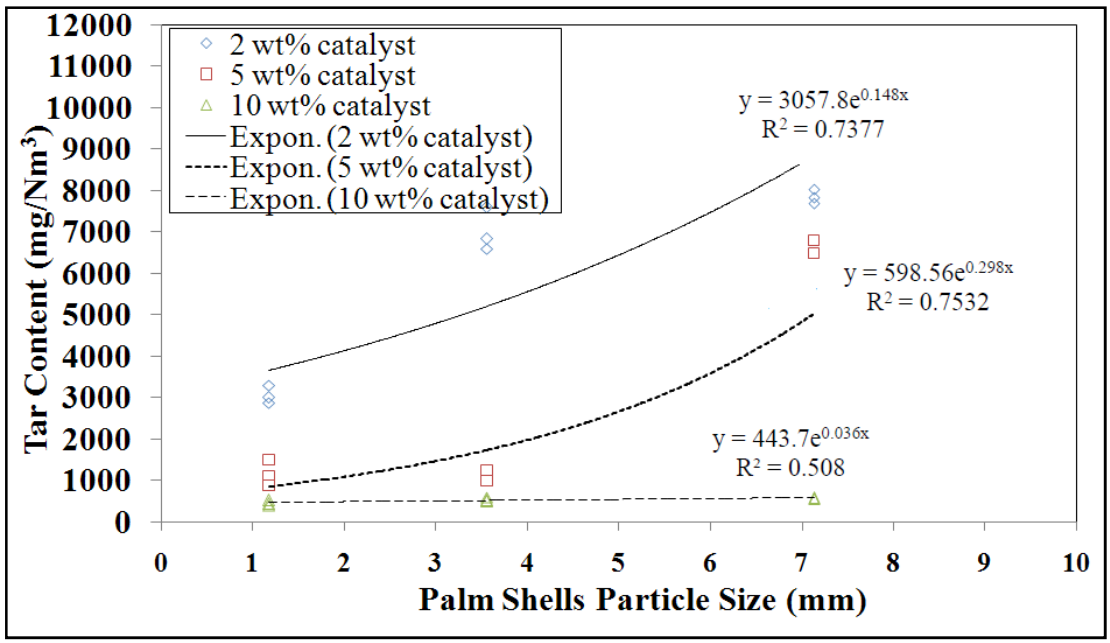


Figure 4.20: Tar content versus palm shells particle size at 3 LPM.

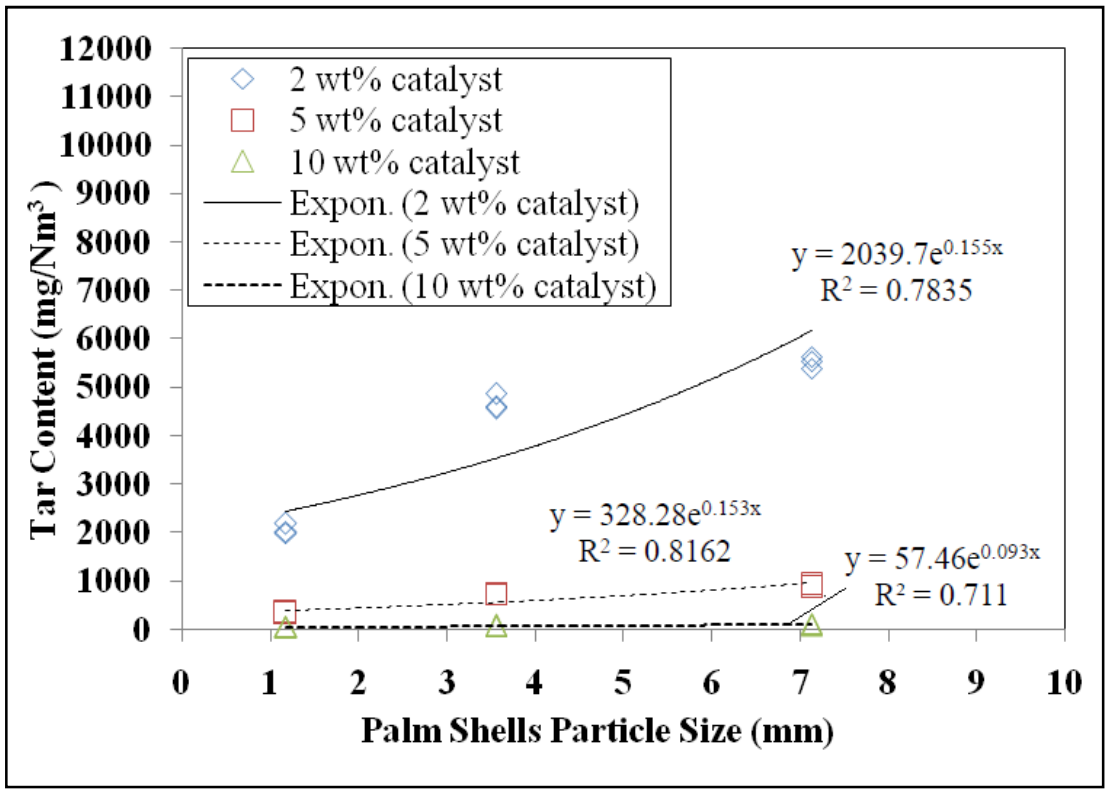


Figure 4.21: Tar content versus palm shells particle size at 5 LPM.

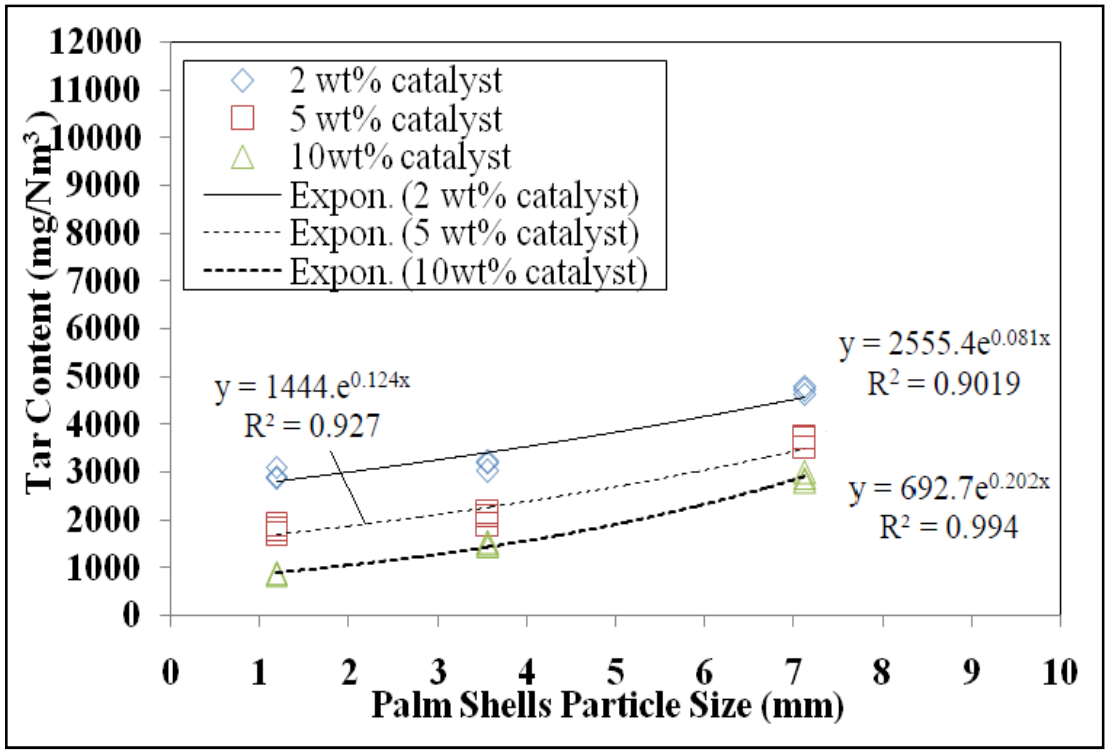


Figure 4.22: Tar content versus palm shells particle size at 7 LPM.

4.3.3 Effect of Oxygen to Nitrogen Ratio

Figure 4.23 to 4.25 show the effect of the ratio of oxygen to nitrogen content with respect to the tar content when palm shells particle size of 1.18 mm used.

Figure 4.23, does not show much change in the tar content as the ratio of oxygen to nitrogen content increased for the 2 weight % catalyst. The tar content is within 6 % change when the ratio of oxygen to nitrogen supplied to the gasifier is from 0.10 to 0.15, which is between 2603 to 2767 mg/Nm^3. The tar content shows a moderate decreasing trend for both 5 and 10 weight % catalyst. The tar content reduced up to 2 and 3 times for 5 and 10 weight % catalyst respectively as the ratio of oxygen to nitrogen is increased.

In Figure 4.24, a strong increasing trend is shown in the tar content for 2 weight % catalyst load whereas a weak decreasing trend is shown for both 5 and 10 weight % catalyst when palm shells particle size of 3.56 mm is used. For the 2 weight % catalyst, the tar content increased up to 2 times as the ratio of oxygen to nitrogen content increased from 0.10 to 0.15. Meanwhile, the tar content reduced almost up to 2 times for the 5 weight % and 10 weight % catalyst.

In Figure 4.25, a strong increasing trend is shown in the tar content for both 2 and 5 weight % catalyst but a gradually decreasing trend is observed for 10 weight % catalyst when palm shells particle size of 7.13 mm used. The tar content increased ~1.6 times as the ratio of oxygen to nitrogen increased from 0.10 to 0.15 when 2 weight % of catalyst is load whereas for the 5 weight % catalyst, the tar content increased up to 2 times. In 10 weight % catalyst, the tar content decreased 3 times as the ratio of oxygen to nitrogen increased from 0.10 to 0.15. This could be further explained that the tar content is heavily dependent on the temperature when compared with the percentage catalyst used in the system. However, when no catalyst is used, the tar content decreased 5 times when the ratio of oxygen to nitrogen increased from 0.10 to 0.15 using this palm shells particle size.

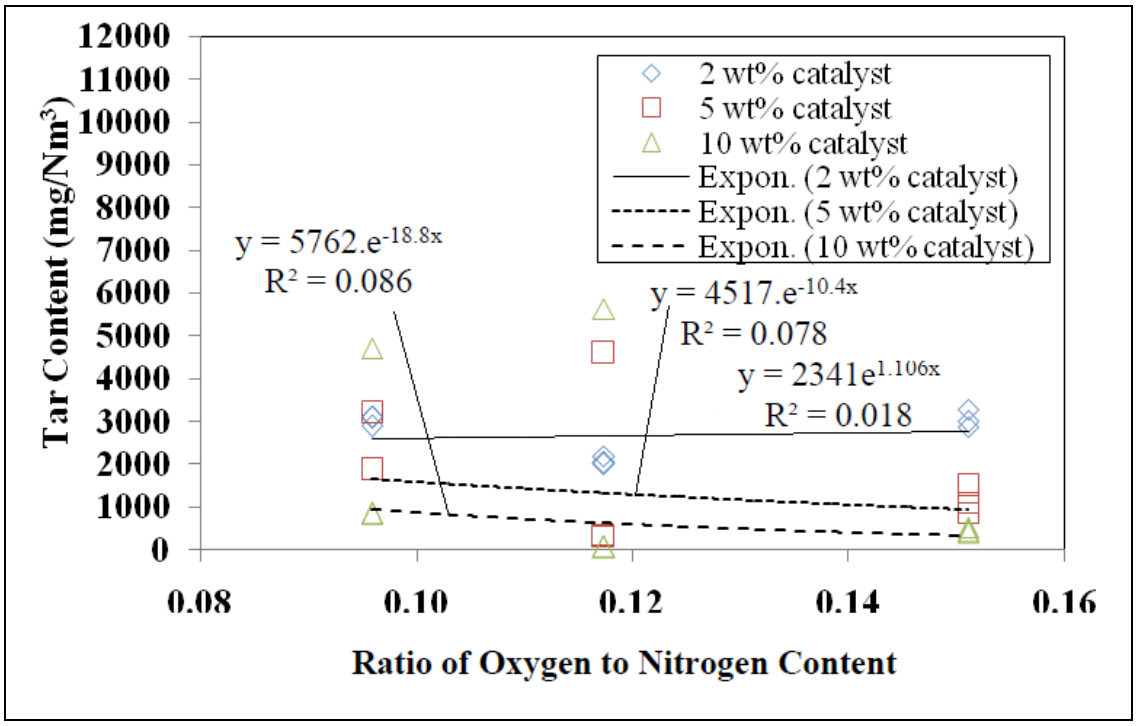


Figure 4.23: Tar content versus ratio of oxygen to nitrogen content using palm shells particle size of 1.18 mm.

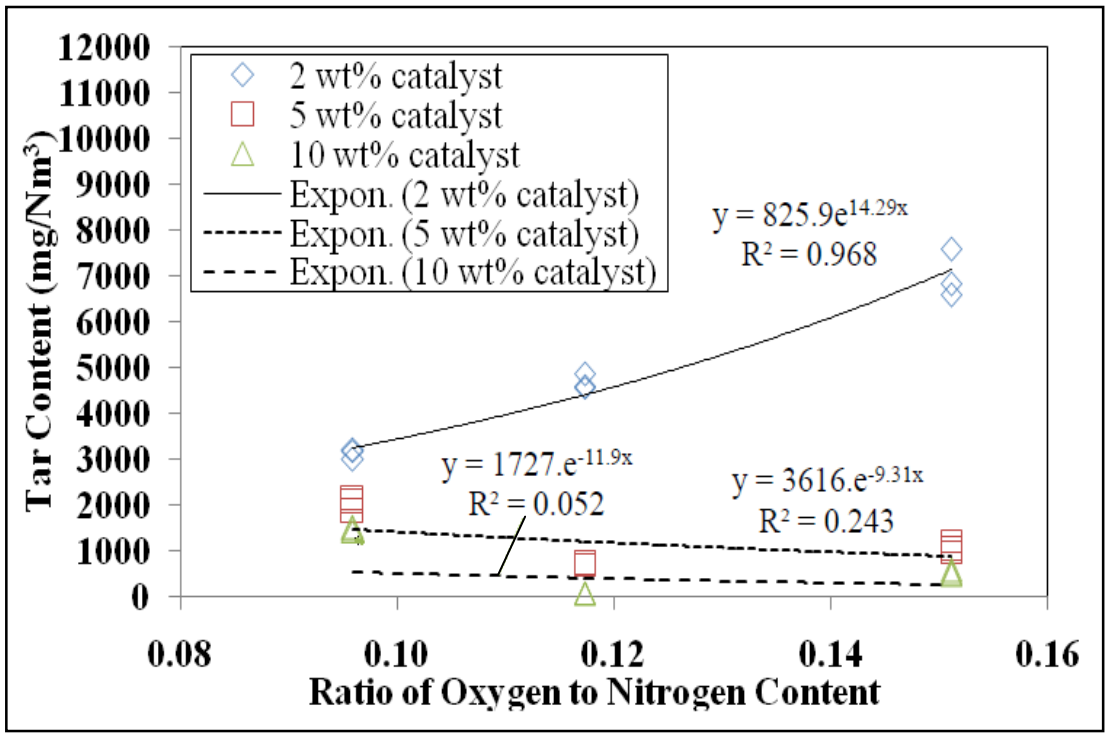


Figure 4.24: Tar content versus ratio of oxygen to nitrogen content using palm shells particle size of 3.56 mm.

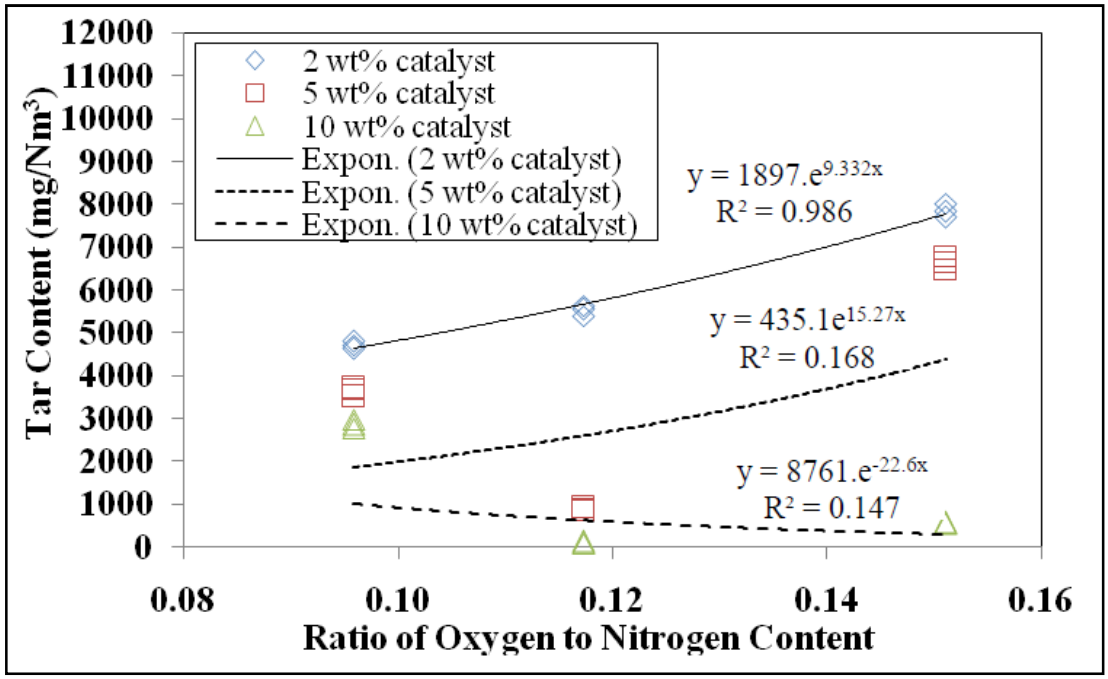


Figure 4.25: Tar content versus ratio of oxygen to nitrogen content using palm shells particle size of 7.13 mm.

4.4 VERIFICATION OF DEVELOPED EQUATIONS FOR THE TAR REMOVAL CLEANUP FOR SYNGAS DERIVED FROM BIOMASS OIL PALM SHELLS

The equations developed from the interpolation of the graphs from Figure 4.17 to Figure 4.25 were verified. It is found that the equations developed for this system has the error of less than 39% for the predicted tar content when verified with the experimental tar content. Therefore, the equations are acceptable for use in the present system for the prediction of tar content at different operating parameters when using HZSM-5 catalyst. In order to achieve less percentage error on the predicted tar content from the developed equations, more experimental readings are required to produce best fitted equations.

Table 4-2: Experimental tar content and predicted tar content value from tar removal equations, and percentage error (ER%) for different palm shells particle size, percentage of HZSM-5 catalyst, nitrogen flowrates and oxygen to nitrogen flowrates.

Weight % Catalyst	*Palm Shells Particle Size (mm)*	*Nitrogen Flowrate (LPM)*	*Ratio of Oxygen to Nitrogen*	*Equations*	*Experimental Tar Content (mg/Nm^3)*	*Predicted Tar Content (mg/Nm^3)*	*ER%*
3	7.13	3	0.15	$y = 21954e^{-0.34x}$	6898	7917	15
6	7.13	3	0.15	(Figure 4.17)	3965	2855	28
3	3.56	3	0.15	$y = 8897e^{-0.30x}$	5201	3617	30
6	3.56	3	0.15	(Figure 4.17)	984	1470	33
3	1.18	3	0.15	$y = 4347e^{-0.23x}$	1986	2180	10
6	1.18	3	0.15	(Figure 4.17)	1358	1094	19
3	7.13	5	0.12	$y = 12519e^{-0.48x}$	2641	2966	12
6	7.13	5	0.12	(Figure 4.18)	1108	703	36
3	3.56	5	0.12	$y = 10913e^{-0.49x}$	2387	2509	5
6	3.56	5	0.12	(Figure 4.18)	798	577	28
3	1.18	5	0.12	$y = 3981e^{-0.42x}$	1350	1129	16
6	1.18	5	0.12	(Figure 4.18)	286	320	12
3	7.13	7	0.10	$y = 5164e^{-0.06x}$	3784	4313	14
6	7.13	7	0.10	(Figure 4.19)	3145	3603	15
3	3.56	7	0.10	$y = 3535e^{-0.09x}$	3045	2699	11
6	3.56	7	0.10	(Figure 4.19)	2678	2060	23
3	1.18	7	0.10	$y = 3947e^{-0.15x}$	2788	2517	10
6	1.18	7	0.10	(Figure 4.19)	1429	1605	12
2	0.59	3	0.15	$y = 3057e^{0.148x}$ (Figure 4.20)	2985	3336	12
5	0.59	3	0.15	$y = 598.5e^{0.298x}$ (Figure 4.20)	1058	714	33
10	0.59	3	0.15	$y = 443.7e^{0.036x}$ (Figure 4.20)	1201	782	35
2	0.59	5	0.12	$y = 2039e^{0.155x}$ (Figure 4.21)	2569	2234	13
5	0.59	5	0.12	$y = 328.2e^{0.153x}$ (Figure 4.21)	569	359	37
10	0.59	5	0.12	$y = 57.46e^{0.093x}$ (Figure 4.21)	86	61	29
2	0.59	7	0.10	$y = 2555e^{0.081x}$ (Figure 4.22)	2274	2680	18
5	0.59	7	0.10	$y = 1444e^{0.124x}$ (Figure 4.22)	1798	1554	14

10	0.59	7	0.10	$y = 692.7e^{0.202x}$ (Figure 4.22)	1203	780	35
2	1.18	5	0.12	$y = 2341e^{1.106x}$ (Figure 4.23)	2118	2644	25
5	1.18	5	0.12	$y = 4517e^{-10.4x}$ (Figure 4.23)	1985	1439	28
10	1.18	5	0.12	$y = 5762e^{-18.8x}$ (Figure 4.23)	1198	729	39
2	3.56	5	0.12	$y = 825.9e^{14.29x}$ (Figure 4.24)	3498	3977	14
5	3.56	5	0.12	$y = 3616e^{-9.31x}$ (Figure 4.24)	1047	1299	24
10	3.56	5	0.12	$y = 1727e^{-11.9x}$ (Figure 4.24)	745	466	37
2	7.13	5	0.12	$y = 1897e^{9.332x}$ (Figure 4.25)	7341	5295	28
5	7.13	5	0.12	$y = 435.1e^{15.27x}$ (Figure 4.25)	1987	2333	17
10	7.13	5	0.12	$y = 8761e^{-22.6x}$ (Figure 4.25)	1174	729	38

4.5 CONCLUSIONS

In this chapter, (i) the results of gas chromatography analysis on the biomass palm shells tar produced, (ii) influences of nitrogen flowrate and particle size on the biomass gasification index (BGI), tar content, emissions of CO, NO, and SO_2, and percentage of HZSM-5 catalysts, (iii) development and verification equations are represented for the tar removal cleanup for syngas derived from biomass oil palm shells.

Gas chromatography analysis is carried out on the tar samples produced from the gasification of biomass palm shells in different oxygen to nitrogen ratio and percentage of HZSM-5 catalyst. The chemical components detected in each tar sample are quantified in volume percentage.

For the effect of different oxygen to nitrogen ratio used, it is observed that the tar contains a high concentration of carbolic acid approximately 5 to 8 volume % of the gas in the range of oxygen to nitrogen flowrate studied. The carbolic acid concentration decreases in the tar produced when the oxygen to nitrogen ratio is increased. The overall heterocyclic aromatics in the tar content are comparable when operating with oxygen to nitrogen ratio of 0.12 and 0.15. Since majority of the tar components are classified under heterocyclic aromatics, these chemical components exhibits high water solubility (Devi 2005, 36) and lead to an increase in tar dewpoint aggravating tar condensation and aerosol formation (Paasen and Kiel 2004, 3). Therefore, it is highly encouraged to eliminate the tar rather than disposing it as waste liquid stream.

For the effect of different percentage of HZSM-5 catalyst, it is observed that the carbolic acid had significantly reduced with the presence of HZSM-5 catalyst. The lowest concentration of carbolic acid can be achieved when using 5 weight % of HZSM-5 catalyst and operating in both oxygen to nitrogen ratio of 0.10 and 0.15.

*As it was stated above, it is most convenient when studying this effect to represent oxygen and nitrogen flow rate in terms of LPM, rather than their ratio.

The reduction of 99% and 79 volume % carbolic acid obtained when comparing without the presence of HZSM-5 catalyst when oxygen to nitrogen ratio supplies of 0.10 and 0.15 respectively. Besides that, as the percentage of the catalyst increased, less chemical compounds are found in the tar which means that most of the chemical components in the tar had been eliminated. It can be concluded that HZSM-5 can be recommended to be used in the system.

Next, the influences on the biomass gasification index (BGI), tar content, emissions of CO, NO, and SO_2, and percentage of HZSM-5 catalysts are studied against nitrogen flowrate and palm shells particle size which are carried out statistically using Minitab (v. 15) software to detect the factor and interaction effects which are important in this study. The independent variables involved in this study are average palm shells particle size, nitrogen flow rate, and weight percentage of calcined HZSM-5 catalyst.

It is observed that palm shells particle size has a significant effect on the BGI in the range of variable studied. Higher BGI could be obtained if larger palm shells particle size is used in this system. It is observed that palm shells particle size of 1.18 mm tends to agglomerate compared with palm shells particle size of 3.56 mm and 7.13 mm. Therefore, the surface area of particle size of 1.18 mm tends to decrease and the heating rate slow down and the BGI is lowered compared with the two other palm shells particle sizes. Bed agglomeration occurred is mainly due to the main reason of the condensation of alkali species in the biomass ash on the particle surface (Liu et al. 2009, 6505).

Nitrogen flowrate and palm shells particle size have significant effects on the tar content. The tar content increases if nitrogen flowrate is increased or larger palm

shells particle size is used. This can be further explained when the nitrogen flowrate is increased, the oxygen concentration in the gas mixture decreased which will influence the decrease in temperature and lead to less cracking reactions of the tar in the reactors (Aznar et al. 2008). In the effect of palm shells particle size on the tar content, smaller palm shells particle size produce lesser tar compared to larger palm shells particle size because diffusion of the volatiles from smaller particles is faster and the cracking process becomes less severe than in the case of particles with a larger size (Padban et al. 2000). It is found that the operating parameters that produced tar content within the gas turbine limit (<100-500 mg/Nm^3) without using calcined HZSM-5 catalyst are oxygen to nitrogen ratio of 0.12 and using palm shells particle size of 1.18 mm. Meanwhile, with calcined HZSM-5 catalyst, the operating parameters that produced tar content within the gas turbine limit are using any palm shells particle sizes of 1.18 mm, 3.56 mm, or 7.13 mm and supplying either 0.12 or 0.15 of oxygen to nitrogen ratio when using 10 weight% calcined HZSM-5 catalyst. For operating parameters that did not achieved tar content within the gas turbine limit, an external catalytic cracker unit can be suggested to be installed after the gasifier or a higher percentage of HZSM-5 catalyst greater than 10% used on the existing experimental setup.

Nitrogen flow rate has the most significant effects on the CO production compared to palm shells particle size. Lower CO emissions produced when higher nitrogen flow rate has been used. As mentioned lower nitrogen flowrate will increased the temperature of the system due to the increased of oxygen concentration in the mixture of the gases, which gives a good agreement with Boudouard reaction which is an endothermic reaction where temperature favours the product, CO rather than the reactants, C and CO_2.

On the NO production, nitrogen flow rate has the most significant effects compared to palm shells particle size. Generally, when the nitrogen flow rate increased, the NO production also increased. Besides that, a minimal amount of nitrogen is released

from the palm shells during the devolatilisation stage.

Both nitrogen flow rate and palm shells particle size does not have any significant effects on the SO_2 production and it is not considered to be a problem since biomass feeds have a very low sulphur contents (Bridgwater 1995, 642).

Lastly, equations developed for the tar removal cleanup for syngas derived from biomass oil palms shells from the interpolation of the graphs are verified to ensure whether the equations are acceptable for use in the present system for the prediction of tar content at different operating parameters when using HZSM-5 catalyst. It is found that the error is less than 39% for the predicted tar content obtained within the when verified with the experimental tar content. Therefore, the equations are acceptable for the prediction of tar content at different operating parameters when using HZSM-5 catalyst.

Chapter 5 Conclusions and Recommendations

5.1 CONCLUSIONS

Biomass palm shells is one of the favourable bioenergy sources due to the growing global demand for edible oil which has resulted in oil palm to become today world's largest source of edible oil with 38.5 million tonnes or 25% of the world edible oil and fat production. Hence, it was estimated that oil palm biomass generated in Malaysia was about 55.73 million tonnes in year 2005.

Presently, the most common methods of handling this biomass is either to burn them with energy recovery (combustion) or landfilling which results to a considerable source of atmospheric pollutants. Therefore, the implementation of biomass gasification would be one of the most promising approaches in treating solid waste product and as source of renewable energy. Through biomass gasification, biomass can be converted into syngas containing but also several undesired contaminants such as tars, ammonia, and particulates that must be controlled to avoid plugging and damaging of the downstream equipment. Therefore, to use this gas in gas engines and gas turbines, in addition to have a design and optimised operation of the biomass gasifier, there is need for cleaning and upgrading the gasification gas. Catalytic hot gasification gas cleaning is an interesting and promising method for tar elimination, as well as the ammonia, rather than transferring them to waste liquid stream that is very difficult to dispose. Catalytic cracking is selected to be used rather than thermal cracking as this method does not required as high temperature compared with thermal cracking which could save operating cost in this system and also the cracking reaction increases the yield of improved quality products at a lower temperature.

In this research, HZSM-5 catalyst is selected as a catalyst for hot gas clean up in the

fixed bed reactor since it has been used as a catalyst for fluid catalytic cracking (FCC) units in oil refineries for the increase the motor octane of gasoline, increase the total liquefied petroleum gas (LPG) and increase the olefin content of the fraction. Therefore, it will be worthwhile to study the catalytic cracking effect of this catalyst on the tar produced from biomass palm shells gasification.

The experimental conditions examine range from the average palm shells particle size of 1.18-7.13 mm; nitrogen flow rate of 3-7 LPM; and percentage of HZSM-5 catalyst of 2-10 weight %. The air flow rate is kept constant at 5 LPM to the inlet of the reactor.

There are three main parts in this studies which are (i) gas chromatography analysis on the biomass palm shells tar produced, (ii) influences on the biomass gasification index (BGI), tar content, emissions of CO, NO, and SO_2, and percentage of HZSM-5 catalysts, (iii) development and verification of equations for the tar removal cleanup for syngas derived from biomass oil palm shells. The findings are summarised as below:

(i) Gas chromatography analysis on the biomass palm shells tar produced

For the effect of different oxygen to nitrogen ratio used, is observed that the tar contains high concentration of carbolic acid approximately 5 to 8 volume% of the gas in the range of oxygen to nitrogen flow rate studied. The carbolic acid concentration decreases in the tar produced when higher oxygen content in the gas mixtures supplies. The overall heterocyclic aromatics in the tar content are comparable when operating with oxygen to nitrogen ratio of 0.12 and 0.15.Since majority of the tar components are classified under heterocyclic aromatics, these chemical components exhibits high water solubility (Devi 2005, 36) and lead to an increase in tar dewpoint aggravating tar condensation and aerosol formation (Paasen and Kiel 2004, 3). Therefore, it is highly encouraged to eliminate the tar rather than disposing it as waste liquid stream.

For the effect of different percentage of HZSM-5 catalyst, it is observed that the

carbolic acid had significantly reduced with the presence of HZSM-5 catalyst. The lowest concentration of carbolic acid can be achieved when using 5 weight % of HZSM-5 catalyst and operating in both oxygen to nitrogen ratio of 0.10 and 0.15. The reduction of 99% and 79% carbolic acid is obtained when comparing the operating condition without the presence of HZSM-5 catalyst and when oxygen to nitrogen ratio supplies of 0.10 and 0.15 respectively. Besides that, as the percentage of the catalyst increased, less chemical compounds are found in the tar which means that most of the chemical components in the tar had been eliminated. It can be concluded that HZSM-5 proven efficient to be used in the system at the percentage of 5% catalyst load by weight.

(ii) Influences of nitrogen flowrate and particle size on the biomass gasification index (BGI), tar content, emissions of CO, NO, and SO_2, and percentage of HZSM-5 catalysts

It is observed that palm shells particle size has a significant effect on the BGI in the range of variable studied. Higher BGI could be obtained if larger palm shells particle size is used in this system. It is observed that palm shells particle size of 1.18 mm tends to agglomerate compared with palm shells particle size of 3.56 mm and 7.13 mm. Therefore, the surface area of particle size of 1.18 mm tends to decrease and the heating rate slow down and the BGI is lowered compared with the two other palm shells particle sizes. In another words, larger palm shells particle size are easier to be burnt compared to smaller palms shells particle size. The main reason for bed agglomeration to occur is due to the condensation of alkali species in the biomass ash on the particle surface (Liu et al. 2009, 6505).

As to tar content, mixture of air to nitrogen supplied and palm shells particle size have significant effects. The tar content increases if nitrogen flowrate is increased or larger palm shells particle size is used. This can be further explained when the nitrogen flowrate is increased, the oxygen concentration in the gas mixture is decreased which will influence the decrease in temperature and leads to less cracking

reactions of the tar in the reactors (Aznar et al. 2008). For the effect of palm shells particle size on the tar content, smaller palm shells particle size produce lesser tar compared to larger palm shells particle size because diffusion of the volatiles from smaller particles is faster and the cracking process becomes less severe than in the case of particles with a larger size (Padban et al. 2000). It is found that the operating parameters that produced tar content within the gas turbine limit (<100-500 mg/Nm^3) without using calcined HZSM-5 catalyst are oxygen to nitrogen ratio of 0.12 and using palm shells particle size of 1.18 mm. Meanwhile, with calcined HZSM-5 catalyst, the operating parameters that produced tar content within the gas turbine limit are using any palm shells particle sizes of 1.18 mm, 3.56 mm, or 7.13 mm and supplying either 0.12 or 0.15 of oxygen to nitrogen ratio when using 10% calcined HZSM-5 catalyst.

The ratio of oxygen to nitrogen has the most significant effects on the CO production compared to palm shells particle size. Lower CO emission produced when lower oxygen content in gas mixture is used. As mentioned, higher oxygen to nitrogen ratio will increase the temperature of the system due to the increased of oxygen concentration in the mixture of the gases, which gives a good agreement with Boudouard reaction which is an endothermic reaction where temperature favours the product, CO rather than the reactants, C and CO_2.

On the NO production, the ratio of oxygen to nitrogen flow rate has the most significant effects compared to palm shells particle size. Generally, when the ratio of oxygen to nitrogen flow rate decreased, the NO production also increased. Besides that, a minimal amount of nitrogen is released from the palm shells during the devolatilisation stage.

Both the content of the mixture of nitrogen and air supplied to the reactor and palm shells particle size does not have any significant effects on the SO_2 production and it is not considered to be a problem since biomass feeds have a very low sulphur

contents (Bridgwater 1995, 642).

(iii) Develop and verification of models for the tar removal cleanup for syngas derived from biomass oil palm shells

Suitable correlations for the tar removal cleanup for syngas derived from biomass palm shells at different operating parameters when using HZSM-5 catalyst have been developed from the interpolation of the experimental data obtained in the accuracy of 39%. The correlations are acceptable to be used in the present system for the prediction of tar content at different operating parameters when using HZSM-5 catalyst.

5.2 RECOMMENDATIONS

- It has proven that zeolite HZSM-5 catalyst is suitable to be used in the present system. It would be recommended to scale-up the present experimental setup into pilot scale for future work to determine the efficiency and feasibility of the HZSM-5 catalyst and the amount of eliminating the tar produced from syngas derived palm shells at a higher throughput.

- For operating parameters that did not achieved tar content within the gas turbine limit, an external catalytic cracker unit can be suggested to be installed after the gasifier or higher percentage of HZSM-5 catalyst greater than 10% used on the existing experimental setup for further research.

- It is advisable to replace the existing fixed bed reactor with the fluidised bed reactor in the present system due its many advantages which results most current research have been devoted in this technology and also no studies were carried out to investigate the byproducts produced from palm shells gasification in such reactor. As it was pointed out in our preview, the advantages of using this reactor such as this reactor offers higher throughput capabilities and greater fuel flexibility including the ability to handle

low-density feedstock like undensified crop residues or sawdust (Johansson, Bodlund, and Williams 1989). The most recent studies that had been carried using palm oil waste are palm kernel shell in a bench scale fluidised bed gasifier with 60 mm and 425 mm height (Ghani et al. (2009, 260). The authors investigated the characteristics of gasification of biomass palm kernel shell in terms of gasification temperature, fluidisation ratio, static bed height, and equivalence ratio (mass ratio of air to fuel present during combustion) on gas composition, gas yield and gas heating value.

- It is also necessary to run experiments in a wider range of oxygen to nitrogen ratio. This could provide a more accurate prediction of the tar content from the equations produced from the interpolation of the graphs based on the experimental data in the present system.

References

Abu, E. R. Z., E. A. Bramer, and G. Brem. 2004. Review of catalysts for tar elimination in biomass gasification processes. *Industrial & Engineering Chemistry Research* 43(22): 6911-919.

Agarwal, P. K., and R. D. La Nauze. 1989. Transfer processes local to the coal particles, a review of drying, devolatilisation and mass transfer in fluidised bed combustion. *Chemical Engineering Research and Design* 67(5): 457-80.

Air composition. 2005. http://www.engineeringtoolbox.com/air-composition-d_212.html (accessed June 16, 2010).

Antony, J. 2003. *Design of experiments for engineer and scientists.* Great Britain. Butterworth-Heinemann.

Arvelakis, S., and E. G. Koukios. 2002. Physicochemical upgrading of agroresidues as feedstocks for energy production via thermochemical conversion methods. *Biomass and Bionergy* 22(5): 331-48. Science Direct. www.sciencedirect.com (accessed April 2, 2010).

Arsadullah, M., T. Miyazawa, S. Ito, K. Kunimori, M. Yamada, and K. Tomishige. 2004. Gasification of different biomasses in a dual-bed gasifier system combined with novel catalysts with high energy efficiency. *Applied Catalysis* 267(1):98-102. Science Direct. www.sciencedirect.com (accessed August 31, 2011).

Azali, A., A. B. Nasrin, Y. M. Choo, N. M. Adam, and S. M. Sapuan. 2005. Development of gasification system fuelled with oil palm fibres and shells. *American Journal of Applied Sciences (Special Issue)*:72-5.

Aznar, M., J. J. Manyà, G. García, J. L. Sánchez, and M. B. Murillo. 2008. Influence of freeboard temperature, fluidisation velocity, and particle size on tar production and composition during the air gasification of sewage sludge. *Energy and Fuels*. Science Direct. www.sciencedirect.com (accessed April 2, 2010). *Article in press.*

Babu, S. P. 2006. Task gasification of biomass*, IEA Bioenergy Agreement*. www.gastechnology.org/webroot/downloads/en/IEA/IEAWS1Report5_06rev.pdf (accessed on July 3, 2009).

Balat, M., M. Balat, E. Kirtay, and H. Balat. 2009. Main routes for the thermo-conversion of biomass into fuels and chemicals. Part 1:pyrolysis systems. *Energy conversion and Management* 50 (12): 3147-57. Science Direct. www.sciencedirect.com (accessed April 6, 2010).

Basiron, Y., and K. W. Chan. 2004. The oil palm and its sustainability. *Journal of Oil Palm Research* 16: 1-10.

Basu, P. 2006. *Combustion and gasification of fluidised beds*. United States of America: CRC Press.

Becker, B., and Schetter, B. 1992. Gas turbines above 150 MW for integrated coal gasification combined cycles (IGCC). *Journal Engineering Gas Turbines Power* 114(4): 660-664.

Belgiorno, V., G. De Feo, C. Della Rocca, and R.M.A. Napoli. 2003. Energy from gasification of solid wastes. *Waste Management* 23 (1): 1-15. Science Direct.

www.sciencedirect.com (accessed July 16, 2008).

Biomass gasification. 2007. *www.lged-rein.org/knowhow.php?pageid=64* (accessed April 10, 2010).

Biomass Technology Group. 2010. http://www.btgworld.com/ (accessed June 5, 2008).

Boerrigter, H., and R. Rauch 2005. *Review of applications of gases from biomass gasification: Handbook biomass gasification*. Netherlands: Biomass Technology Group.

Bridgwater, A. V. 1994. Catalysis in thermal biomass conversion. *Applied Catalysis A* 116 (1-2): 5-47. Science Direct. www.sciencedirect.com (accessed April 3, 2010).

Bridgwater, A. V. 1995. The technical and economic feasibility of biomass gasification for power generation. *Fuel* 74 (5): 631-53. Science Direct. www.sciencedirect.com (accessed August 18, 2008).

Bridgwater, A. V., A. J. Toft, and J. G. Brammer. 2002. A techno-economic comparison of power production by biomass fast pyrolysis with gasification and combustion. *Renewable and Sustainable Energy Reviews* 6 (3): 181-248. Science Direct. www.sciencedirect.com (accessed July 28, 2008).

Bridgwater, A. V., and G. D. Evans. 1993. An assessment of thermochemical conversion systems for processing biomass and refuse. *ETSU Report B/T1/00207/REP*. UK Department of Trade & Industry.

Buchireddy, P. R., R. M. Bricka, J. Rodriguez, and W. Holmes. 2010. Biomass gasification: catalytic removal of tars over zeolites and nickel supported zeolites. *Energy & Fuels* 24(4): 2707-15.

Chok, V. S., S. Yusup, and A. Gorin. 2009. *Palm Oil International Palm Oil Congress (PIPOC), November 9-12, 2009: Palm shell gasification in pilot scale compartmented fluidised bed gasifier: preliminary high temperature performance and challenges*. Malaysia.

Chuah, T. G., A. G. K. Wan Azlina, Y. Robiah, and R. Omar. 2006. Biomass as the renewable energy sources in Malaysia: an overview. *International Journal of Green Energy* 3 (3): 323-46.

Ciferno, J. P., and J. J. Marano. 2002. Benchmarking biomass gasification technologies for fuels, chemicals, and hydrogen production. *U.S. Department of Energy National Energy Technology Laboratory.* DOE- National Energy Technology Laboratory. http://www.netl.doe.gov (accessed August 25, 2008).

CopperInfo. 2010. *Copper properties*. http://www.copperinfo.com/ (accessed May 31, 2010).

Corella, J., J. M. Toledo, R. Padilla. 2004. Catalytic hot gas cleaning with monoliths in biomass gasification in fluidized beds 1. Their effectiveness for tar elimination. *Industrial & Engineering Chemistry Research* 43(26): 2433-445.

Corella, J., M. A. Caballero, and M. P. Aznar. *Proceedings of the 1st World Conference on Biomass for Energy and Industry, 2000: A 6-lump model for the kinetics of the catalytic tar removal in biomass gasification*.

Dayton, D. 2002. Milestone completion report - A review of the literature on catalytic biomass tar destruction. *United States of America: National Renewable Energy Laboratory (NREL).*

Devi, L. 2005. Catalytic removal of biomass tars; Olivine as prospective in-bed

catalyst for fluidised bed biomass gasifiers. PhD diss. Eindhoven University of Technology. http://alexandria.tue.nl/extra2/200510623.pdf (accessed May 20, 2010).

Diebold, J., D. C. Elliot, A. V. Bridgwater, Y. Solantausta, and D. Beckman. 1994. *Assessment of liquefaction and pyrolysis systems.* IEA Bioenergy Agreement.

DOE. 2004. *Bio-energy*. http://www.eere.energy.gov/consumerinfo/factsheets/nb2.html (accessed June 13, 2009).

Energy research Centre of the Netherlands. n.d. *Tar measurement standard.* www.ecn.nl/ (accessed November 16, 2010).

Elliot, D. C. 1988. *ACS Symposium Series, 1988: Relation of reaction time and temperature of chemical composition of pyrolysis oils*. Washington D. C.: American Chemical Society.

Evans R. J., R. A. Knight, M. Onischak, and S. P. Babu. 1986. *Proceedings Conference Energy from Biomass and Wastes*, *1986: Process performance and environmental assessment of the Renugas process.* Washington D.C.: Institute of Gas Technology.

Gaur, S., and T. Reed. 1998. Thermal data for natural and synthetic fuels. *Marcel Dekker*.

Ghani, W. A. W. A. K, N. A. Alias, A. B. Salleh, M. A. M. Omar, R. Ali, and A. Idris. 2007. *21st Symposium of Malaysia Chemical Engineers (SomChE)*, *December 11-13, 2007: Characterisation of agricultural waste as biofuels: Significance and impact.* Malaysia.

Ghani, W. A. W. A. K., R. A. Moghadam, M. A. M. Salleh, and A. B. Alias. 2009. Air gasification of agricultural waste in a fluidised bed gasifier: hydrogen production performance. Energies 2: 258-68. MDPI Publishing. www.mdpi.com/journal/energies.

Han, J., and H. Kim. 2006. The reduction and control technology of tar during biomass gasification/pyrolysis: an overview. *Renewable and Sustainable Energy Review* 12(2): 397-416. Science Direct. www.sciencedirect.com (accessed May 23, 2010).

Hashem, A., R. A. Akasha, A. Ghith, and D. A. Hussein. 2007. Adsorbent based on agricultural wastes for heavy metal and dye removal: a review. *Energy Education Science Technology* 19: 69-86.

Hasler, P., and T. Nussbaumer. 1999. Sampling and analysis of particles and tar from biomass gasifiers. *Biomass and Bioenergy* 18(1): 61-6. Science Direct. www.sciencedirect.com (accessed May 23, 2010).

Hutchison, F. H. 2009. *Facts about gasification.* http://www.clean-energy.us/facts/gasification.htm (accessed Feb 5, 2010).

Islam, M. N., R. Zailani, and F. N. Ani. 1999. Pyrolytic oil from fluidised bed pyrolysis of oil palm shell and its characterisation. *Renewable Energy* 17(1): 73-84.

Johansson, T. B., B. Bodlund, and R.H. Williams. 1989. *Electricity: efficient end-use and new generation technologies and their planning implications*. Lund University Press. Quoted in Williams and Larson, 1996,159.

Juniper 2000. *Pyrolysis & gasification of waste.* Worldwide Technology & Business Review. Juniper Consultancy Services Ltd.

Kaltschmitt, M., and C. Rösch, Research Report AIR CT94-2284, IER, Universität Stuttgart, 1998.

Kiel, J. H. A., S. V. B. Van Paasen, and J. P. A. Neeft 2004. Primary measures to reduce tar formation in fluidised-bed biomass gasifiers. *Final Report SDE Project P1999-012.* ECN Biomass.

Kurkela, E., and P. Ståhlberg. 1992. Air gasification of peat, wood and brown coal in a pressurised fluidised-bed reactor. i. Carbon conversion, gas yields and tar formation. *Fuel Processing Technology* 31 (1): 1-21. Science Direct. www.sciencedirect.com (accessed May 21, 2009).

Kutner, N. H., C. J. Nachtsheim, J. Neter, and W. Li. 2004. *Applied linear statistical model.* Boston: Mc-Graw Hill.

Lahijani, P., and Z. A. Zainal. 2010. Gasification of palm empty fruit bunch in a bubbling fluidized bed: a performance and agglomeration study. *Bioresource Technology* . Science Direct. www.sciencedirect.com (accessed November 24, 2010).

Langston, L. S. and G. J. Opdyke. 1997. Introduction to gas turbines for non-engineers. *Global Gas Turbine News* 37(2). ASME. http://asme.org (accessed December 8, 2010).

Leppälahti, J., and E. Kurkela. 1991. Behaviour of nitrogen compounds and tars in fluidised bed air gasification of peat. *Fuel* 70 (4): 491-7. Science Direct. www.sciencedirect.com (accessed May 21, 2009). *Article in press.*

Leppälahti, J., and T. Koljonen 1995. Nitrogen evolution from coal, peat and wood

during gasification: literature review. *Fuel Processing Technology* 43 (1): 1-45. Science Direct. www.sciencedirect.com (accessed September 10, 2009).

Leung, D. Y. C., X. L. Yin, and C. Z. Wu. 2004. A review on the development and commercialisation of biomass gasification technologies in China. *Renewable & Sustainable Energy Reviews* 8 (6): 565-80. Science Direct. www.sciencedirect.com (accessed July 28, 2008).

Levenspiel, O. 2005. What will come after petroleum? *Industrial Engineering Chemistry Research* 44(6): 5073-8.

Lin, W. 2005. Experimental study on the effects of operational parameters of a downdraft gasifier. MSc Thesis., Mississippi State University. http://www.docstoc.com/docs/2368261/EXPERIMENTAL-STUDY-ON-THE-EFFECTS-OF-OPERATIONAL-PARAMETERS-OF-A (accessed August 3, 2008).

Liu, H., Y. Feng, S. Wu, and D. Liu. 2009. The role of ash particles in the bed agglomeration during the fluidised bed combustion of rice straw. *Bioresource Technology* 100 (24): 6505-13. Science Direct. www.sciencedirect.com (accessed November 24, 2010).

Mäkinen, T., J. Leppälahti, E. Kurkela, and Y. Solantausta. 1995. *Proceedings 8th European Conference on Biomass for Energy, Environment, Agriculture, and Industry, October 3-5, 1994: Electricity production from biomass by gasification and a solid oxide fuel cell.* Vienna: Pergamon.

Maniatis, K. 2001. Progress in biomass gasification: an overview. *Oxford: Blackwell*. http://ec.europa.eu/energy/res/sectors/doc/bioenergy/km_tyrol_tony.pdf (accessed July 29, 2008).

McKendry, P. 2002a. Energy production from biomass (part 1): overview of biomass. *Bioresource Technology* 83 (1): 37-46. Science Direct. www.sciencedirect.com (accessed July 16, 2008).

McKendry, P. 2002b. Energy production from biomass (part 3): Gasification technologies. *Bioresource Technology* 83(1): 55-63. Science Direct. www.sciencedirect.com (accessed July 17, 2008).

Milne, T. A., R. J. Evans, and N. Abatzoglou 1998. Biomass gasifier "tars": their nature, formation, and conversion. *NREL Renewable Energy Laboratory.* U.S. Department of Energy. www.osti.gov/ (accessed November 25, 2009).

Mohan, D., C. U. Pittman, and P. H. Steele. 2006. Pyrolysis of wood/biomass for bio-oil: a critical review. *Energy and Fuels* 20 (3). 848-89. Science Direct. www.sciencedirect.com (accessed April 6, 2010).

MPOB. 2007. *A summary of the performance of the Malaysian oil palm industry.* http://econ.mpob.gov.my/ (accessed April 2, 2010).

MPOC. 2008. *World's oil production in 2007.* http://www.mpoc.org.my/ (accessed April 1, 2010).

Murakami, T., G. Xu, T. Suda, Y. Matsuzawa, H. Tani, and T. Fujimori. 2007. Some process fundamentals of biomass gasification in dual fluidised bed. *Fuel* 86 (1-2): 244-55. Science Direct. www.sciencedirect.com (accessed July 12, 2008).

Ni, M., Y. C. Leung, M. K. H. Leung, and K. Sumathy 2006. An overview of hydrogen production from biomass. *Fuel Processing Technology* 87 (5): 461-72. Science Direct. wwww.sciencedirect.com (accessed April 5, 2010).

Olah, G. A., and A. Molnár. 2003. *Hydrocarbon chemistry*. United States of America. John Wiley & Sons.

Padban, N., W. Y. Wang, Z. C. Ye, I. Bjerle, and I. Odenbrand. 2000. Tar formation in pressurised fluidised bed air gasification of woody biomass. *Energy and Fuels* 14(3): 603-11. Chemical Engineering Research Information Center (CHERIC). http://www.cheric.org/ (accessed September 2, 2009).

Pérez, P., M. P. Aznar, M. A. Caballero, J. Gil, J. A. Martin, J. Corella. 1997. Hot gas cleaning and upgrading with a calcined dolomite located downstream a biomass fluidised bed gasifier operating with steam-oxygen mixtures. *Energy and Fuels* 11: 1194-203.

Ragnar, W. 2000. Gasification of biomass: comparison of fixed bed and fluidised bed gasifier. *Biomass & Bioenergy* 18 (6): 489-97. Science Direct. www.sciencedirect.com (accessed August 10, 2008).

Saastamionen, J. J. 1994. *Biomass Combustion Conference*, *Fundamentals of biomass drying, pyrolysis, and combustion.* Cambridge: IEA.

Sadeghbeigi, R. 2000. *Fluid catalytic cracking handbook.* United States of America: Butterworth Heinemann.

Safitri, A. 2005. Biomass gasification using bubbling fluidised-bed gasifier: investigation of the effect of different catalysts on tar reduction. MSc Thesis., Technishe Universiteit Eindhoven. www.tue.nl/ (accessed December 22, 2009).

Saxena, R. C., D. Seal, S. Kumar, and H. B. Gopal. 2008. Thermo-chemical routes for hydrogen rich gas from biomass: a review. *Renewable & Sustainable Energy Reviews* 12(7): 1909-27. Science Direct. www.sciencedirect.com (accessed

December 12, 2009).

Scherzer, J., and A. J. Gruia. 1996. *Hydrocarking Science and Technology*. Oxford: Taylor & Francis Incorporation.

Shuit, S. H., K. T. Tan, K. T. Lee, and A. H. Kamaruddin. 2009. Oil palm biomass as a sustainable energy source: a Malaysian case study. *Energy* 34(9): 1225-35. Science Direct. www.sciencedirect.com (accessed October 12, 2009).

Simell, P., P. Ståhlberg, E. Kurkela, J. Albrecht, S. Deutsch, and K. Sjöström. 2000. Provisional protocol for the sampling and analysis of tar and particulates in the gas from large-scale biomass gasifiers. version 1998. *Biomass and Bioenergy* 18(1): 19-38. Science Direct. www.sciencedirect.com (accessed June 21, 2009).

Stevens, D. J. 2001. Hot gas conditioning: recent progress with larger-scale biomass gasification systems. *NREL Renewable Energy Laboratory.* U.S. Department of Energy. www.osti.gov (accessed November 25, 2009).

Subramaniam, V., C. M. C. Chow, and A. N. Ma. 2003. Energy database of the oil palm. *Palm Oil Engineering Bulletin* 70: 15-22. Palm Oil Information Online Service. www.palmoilis.mpob.gov.my/ (accessed September 13, 2008).

Sutton, D., B. Kelleher, and R. H. Ross. 2001. Review of literature on catalysts for biomass gasification. *Fuel Processing Technology* 73(3): 155-73. Science Direct. www.sciencedirect.com (accessed April 30, 2010).

Synthesis and characterisation of the zeolite ZSM-5. 1995. Institute for Material Research. http://materials.binghamton.edu (accessed May 2, 2010).

Toledo, J. M., J. Corella, G. Molina. 2006. Catalytic hot gas cleaning with monoliths in

biomass gasification in fluidised beds 4. Performance of an advanced, second generation, two-layers based monolithic reactor. *Industrial and Engineering Chemistry Research* 45(4): 1389-96.

Turn, S.Q. 1999. Biomass integrated gasifier combined cycle technology: Application in the cane sugar industry (part 3). *International Sugar Journal* 101 (1207): 367-74.

Umikalsom, M. S., A. B. Ariff, H. S. Zulkifli, C. C. Tong, M. A. Hassan, and M. I. A. Karim. 1997. The treatment of oil palm empty fruit bunch fibre for subsequent use as substrate for cellulose production by *Chaetomium globosum kunze*. Bioresource Technology. 62: 1-9.

U.S. Department of Agriculture. 2007. *Indonesia and Malaysia palm oil production*. http://www.pecad.fas.usda.gov/ (accessed April 2, 2010).

Van Paasen, S. V. B., and J. J. A. Kiel. 2004. *The 2nd World Conference and Technology Exhibition on Biomass for Energy, Industry and Climate Protection, 10-14 May 2004:* Rome, Italy. Tar formation in fluidised-bed gasification-impact of gasifier operating conditions.

Yong, T. L. K., K. T. Lee, A. R. Mohamed, and S. Bhatia. 2007. Potential of hydrogen from oil palm biomass as a source of renewable energy worldwide. *Energy Policy* 35 (11):5692-5701. Science Direct. www.sciencedirect.com (accessed August 30, 2009).

Wahab, N. M. A., N. M. Mokhtar, and N. A. Ludin. 2005. *Seminar on Harmonised Policy Instruments for the Promotion of Renewable Energy and Energy Efficiency in the ASEAN Member Countries*, *September 6-7, 2005: Options and tools for renewable energy implementation in Malaysia.* Shah Alam, Malaysia.

Werther, J., M. Saenger, E.-U Hartge, T. Ogada, and Z. Siagi. 2000. Combustion of agriculture residues. *Progress in Energy and Combustion Science* 206(1): 1-27. Science Direct. www.sciencedirect.com (accessed August 11, 2008).

Werther, J., T. Ogada, V. A. Borodulya, and V. I. Dikalenko. 1995. *In Proceedings of the Institute of Energy's 2nd International Conference on Combustion and Emission Control, December 4-5, 1995: Devolatilisation and combustion kinetic parameters of wet sewage sludge in a bubbling fluidised bed furnace.* London.

Williams, R. H., and E. D. Larson. 1996. Biomass gasifier gas turbine power generating technology. *Biomass and Bioenergy* 10(2-3): 149-66. Science Direct. www.sciencedirect.com (accessed August 27, 2008).

Yaman, S. 2004. Pyrolysis of biomass to produce fuels and chemical feedstocks. *Energy Conversion and Management* 45(5): 651-71. Science Direct. www.sciencedirect.com (aaccessed April 6, 2010).

Yang, H., R. Yan, T. Chin, D. T. Liang, H. Chen, and C. Zheng. 2004. Thermogravimetric analysis –Fourier transform infrared analysis of palm oil waste pyrolysis. *Energy and Fuels* 18 (6): 1814-21.

Yong, T. L. K., K. T. Lee, A. R. Mohamed, and S. Bhatia. 2007. Potential of hydrogen from oil palm biomass as a source of renewable energy worldwide. *Energy Policy* 35 (11): 5692-701. Science Direct: www.sciencedirect.com (accessed June 5, 2008).

Win, D. T. 2007. Zeolites - earliest solid state acids. *AU Journal of Technology* 11(1): 36-41. AU Journal Assumption University of Thailand. www.journal.au.edu (accessed June 7, 2010).

Zarfolin, S. 1995. Use of crude-bio oil in gas turbine: description of experimental activities and tests results. *Bio-crude Oil Technology*, ENEL.

Zeolite applications. 2009a. *Lenntech*. http://www.lenntech.pl (accessed May 10, 2010).

Zeolite applications. 2009b. *Peng Tai Corporation.* http://www.pengtaiusa.com (accessed May 10, 2010).

Zeolite molecular sieve. 2008. *Xinyuan Molecular Sieve*. www.molecularsieve.org (accessed May 10, 2010).

Zeolyst International. n.d. *ZSM-5.* http://www.zeolyst.com/ (accessed May 30.2010).

Zuberbühler, U., M. Specht, and A. Bandi. 2005. Gasification of biomass- an overview on available technologies. *RENEW- 1st European Summer School on Renewable Motor Fuels*. BAUM Group. http://www.baumgroup.de/ (accessed July 21, 2008).

Appendices

APPENDIX A
MATERIAL SAFETY DATA SHEET (MSDS) FOR ZSM-5 CATALYST

ZEOLYST INTERNATIONAL

MSDS
MATERIAL SAFETY DATA SHEET

Trade Name: **CBV3024E**
ZEOLITE AMMONIUM ZSM-5 POWDER
Date Prepared: **03/14/06** *Page:* **1 of 4**

1. CHEMICAL PRODUCT AND COMPANY IDENTIFICATION

Product name:	**CBV3024E**
Product description:	**ZEOLITE AMMONIUM ZSM-5 POWDER**
Manufacturer:	**Zeolyst International** **P. O. Box 830** **Valley Forge, PA 19482 USA**
Telephone:	**610-651-4200**
In case of emergency call:	**610-651-4200**
For transportation emergency Call CHEMTREC:	**800-424-9300**

2. COMPOSITION/INFORMATION ON INGREDIENTS

Chemical and Common Name	*CAS Registry Number*	*Wt. %*	*OSHA PEL*	*ACGIH TLV*
Zeolite	**1318-02-1**	**100%**	**15mg/m^3 total dust** **5mg/m^3 respirable** **(Particulates Not Otherwise Regulated)**	**10 mg/m^3** **3 mg/m^3 respirable**

3. HAZARDS IDENTIFICATION

Emergency Overview:	**White, odorless, powder. Causes respiratory irritation. Causes mild eye irritation. May cause skin irritation. Ammonia released on contact with strong bases. Noncombustible. Ammonia or nitrogen oxides may be released at high temperatures.**
Eye contact:	**Causes mild eye irritation.**
Skin contact:	**Prolonged or repeated contact may dry skin and cause irritation.**
Inhalation:	**Causes irritation.**
Ingestion:	**No known hazards. Inedible.**
Chronic hazards:	**No known hazards.**
Physical hazards:	**Absorbs water from air and fluids. Generates heat when it absorbs water.**

4. FIRST AID MEASURES

Eye:	**In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Get medical attention if irritation persists.**
Skin:	**In case of contact, immediately flush skin with plenty of water. Remove contaminated clothing and shoes. Get medical attention if irritation develops**

Trade Name: **CBV3024E**
ZEOLITE AMMONIUM ZSM5 POWDER
Date Prepared: **03/14/06** *Page:* **2 of 4**

	and persists. Wash clothing before reuse. Thoroughly clean shoes before reuse.
Inhalation:	**Remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention.**
Ingestion:	**Not applicable.**

5. FIRE FIGHTING MEASURES

Flammable limits:	**This material is noncombustible.**
Extinguishing Media:	**This material is compatible with all extinguishing media.**
Hazards to fire-fighters:	**Ammonia or nitrogen oxides may be released at high temperatures.**
Fire-fighting equipment:	**The following protective equipment for fire fighters is recommended when this material is present in the area of a fire: self-contained breathing apparatus (SCBA), chemical goggles, body-covering protective clothing, chemical resistant gloves, and rubber boots.**

6. ACCIDENTAL RELEASE MEASURES

Personal protection:	**Wear safety goggles, body-covering protective clothing, chemical resistant gloves, and rubber boots, NIOSH-approved dust respirator where dust occurs. See section 8.**
Environmental Hazards:	**Sinks in water. No know environmental hazards.**
Small spill cleanup:	**Carefully shovel or sweep up spilled material and place in suitable container. Avoid generating dust. Use appropriate Personal Protective Equipment (PPE). See section 8.**
Large spill cleanup:	**Keep unnecessary people away; isolate hazard area and deny entry. Do not touch or walk through spilled material. Carefully shovel or sweep up spilled material and place in suitable container. Avoid generating dust. Use appropriate Personal Protective Equipment (PPE). See section 8.**
CERCLA RQ:	**There is no CERCLA Reportable Quantity for this material. If a spill goes off site, notification of state and local authorities is recommended.**

7. HANDLING AND STORAGE

Handling:	**Avoid contact with eyes, skin and clothing. Avoid breathing dust. Keep container closed. Promptly clean up spills. Wash thoroughly after handling.**
Storage:	**Keep containers closed. Store separated from strong bases in original containers or clean metal, plastic, or fiber containers.**

Trade Name: **CBV3024E**
ZEOLITE AMMONIUM ZSM5 POWDER
Date Prepared: **03/14/06** *Page:* **3 of 4**

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Engineering controls:	**Use with adequate ventilation. Safety shower and eyewash fountain should be within direct access.**
Respiratory protection:	**Use a NIOSH-approved dust respirator where dust occurs. Observe OSHA regulations for respirator use (29 C.F.R. §1910.134)**
Skin protection:	**Wear body-covering protective clothing and gloves.**
Eye protection:	**Wear safety goggles.**

9. PHYSICAL AND CHEMICAL PROPERTIES

Appearance:	**White powder.**
Odor:	**Odorless.**
pH:	**Not applicable.**
Specific Gravity:	**>1.**
Solubility in water:	**Negligible.**

10. STABILITY AND REACTIVITY

Stability:	**This material is stable.**
Conditions to avoid:	**None.**
Materials to avoid:	**Ammonia may be released on contact with strong bases.**
Hazardous decomposition products:	**Ammonia, nitrogen oxides.**

11. TOXICOLOGICAL INFORMATION

Acute Data:	**When tested for primary irritation potential, similar materials caused mild eye irritation and were slightly irritating or non-irritating to the skin. Human experience with similar materials indicates that prolonged or repeated contact may dry skin and cause irritation. This material has not been tested for acute inhalation toxicity. It contains fine particles which can cause respiratory irritation. The acute oral toxicity of this material has not been tested. There are currently no reports of human toxicity for ingested zeolite.**
Subchronic Data:	**This material has not been tested for subchronic toxicity potential.**
Special Studies:	**This material has not been tested for chronic inhalation toxicity. Zeolite Beta is not listed by NTP, IARC, or OSHA as a carcinogen.**

Trade Name: **CBV3024E**
ZEOLITE AMMONIUM ZSM5 POWDER
Date Prepared: **03/14/06** *Page:* **4 of 4**

12. ECOLOGICAL INFORMATION

Eco toxicity:	**This material has not been tested for ecotoxicity potential. There are presently no known reports of adverse environmental effects.**
Environmental Fate:	**Does not bioconcentrate in animals.**
Physical/Chemical:	**Sinks in water.**

13. DISPOSAL CONSIDERATIONS

Classification:	**This material is not RCRA Hazardous waste.**
Disposal Method:	**Dispose in accordance with federal, state and local regulations.**

14. TRANSPORT INFORMATION

DOT UN Status:	**This material is not regulated hazardous material for transportation.**

15. REGULATORY INFORMATION

CERCLA:	**See section 6.**
SARA TITLE III:	**This material is not a listed Toxic Chemical subject to the reporting requirements of SARA Title III §313 and 40 C.F.R. Part 372. Hazard Categories under SARA Title III §§311/312: Acute.**
TSCA:	**All ingredients of this material are listed on the TSCA inventory.**

16. OTHER INFORMATION

Prepared by:	**John G. Blumberg**
Supersedes revision of:	**06/01/98**

THE INFORMATION ON THIS SAFETY DATA SHEET IS BELIEVED TO BE ACCURATE AND IT IS THE BEST INFORMATION AVAILABLE TO ZEOLYST INTERNATIONAL. THIS DOCUMENT IS INTENDED ONLY AS A GUIDE TO THE APPROPRIATE PRECAUTIONS FOR HANDLING A CHEMICAL BY A PERSON TRAINED IN CHEMICAL HANDLING. ZEOLYST INTERNATIONAL MAKES NO WARRANTY OF MERCHANTABILITY OR ANY OTHER WARRANTY, EXPRESS OR IMPLIED WITH RESPECT TO SUCH INFORMATION OR THE PRODUCT TO WHICH IT RELATES, AND WE ASSUME NO LIABILITY RESULTING FROM THE USE OR HANDLING OF THE PRODUCT TO WHICH THIS SAFETY DATA SHEET RELATES. USERS AND HANDLERS OF THIS PRODUCT SHOULD MAKE THEIR OWN INVESTIGATIONS TO DETERMINE THE SUITABILITY OF THE INFORMATION PROVIDED HEREIN FOR THEIR OWN PURPOSES.

(MSDS obtained from Zeolyst International (n.d.))

APPENDIX B

GAS CHROMATOGRAPHY DATA FOR BIOMASS PALM SHELLS TAR

Table B-1: Results of gas chromatography analysis on the biomass palm shells tar produced.

No.		1	2	3	4	5	6	7
Average Particle Size (mm)		3.56	3.56	3.56	7.13	7.13	7.13	1.18
Nitrogen Flowrate (LPM)		3	5	7	3	5	7	5
Compressed Air (LPM)		5	5	5	5	5	5	5
Calcined ZSM-5 Catalyst (Weight %)		0	0	0	5	5	5	5
Component Detected (Volume %)	Carbolic Acid	5.18	6.27	8.19	7.15	6.28	5.20	1.06
	o-Methoxy Phenol	2.68	0	0	0	0	0	0
	2-Methoxy p-Cresol	1.19	0	0	0	0	0	0
	Diethyl Phthalate	2.16	2.35	0	0	0	0	0
	1-3-dimethoxy-2-hydroxybenzene	1.24	1.17	0	0	0	0	0
	o-Cresol	0	2.27	1.29	0	0	0	0
	p-Ethylguiacol	0	2.29	1.68	2.29	0	0	0
	o-Guaiacol	0	0	1.16	0	1.16	0	0
	p-Cresol-2-Methoxy	0	0	2.23	0	0	0	0
	p-Methoxylhydroxybenzene	0.00	0.00	0.00	2.61	0.00	0.00	0.00
	2-Methoxyl-5-Methyl Phenol	0.00	0.00	0.00	1.22	0.00	0.00	0.00
	o-Hydroxybenzhydrazide	0.00	0.00	0.00	1.75	0.00	0.00	0.00
	p-Dimethyoxybenzene	0.00	0.00	0.00	0.00	1.45	0.00	0.00
	Phenylacetone Ketomine	0.00	0.00	0.00	0.00	1.17	2.33	0.56
	Phenethyl-2-methylbutyrate	0.00	0.00	0.00	0.00	0.00	0.00	0.41
	1-Methyl-1,4-Cyclohexadiene	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	2-Methoxylpyridine	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	p-Cresol	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Methyl Acetyl Dithiocarbomate	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table B-1 (continued)

No.		8	9	10	11	12	13	14
Average Particle Size (mm)		1.18	3.56	3.56	1.18	1.18	1.18	1.18
Nitrogen Flowrate (LPM)		5	3	3	3	7	7	7
Compressed Air (LPM)		5	5	5	5	5	5	5
Calcined ZSM-5 Catalyst (Weight %)		2	2	5	10	10	5	2
Component Detected (Volume %)	Carbolic Acid	0.00	1.24	1.10	2.61	0.84	0.05	3.16
	o-Methoxy Phenol	0	0	0	0	0	0	0
	2-Methoxy p-Cresol	0	0	0	0	0	0	0
	Diethyl Phthalate	3.49	0	0	0	0	0	5.66
	1-3-dimethoxy-2-hydroxybenzene	0	0	0	0	0	0	0
	o-Cresol	0	0	0	0	0	0	0
	p-Ethylguiacol	0	0	0	0	0	0	0
	o-Guaiacol	0	0	0	0	0	0	1.10
	p-Cresol-2-Methoxy	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	p-Methoxylhydroxybenzene	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	2-Methoxyl-5-Methyl Phenol	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	o-Hydroxybenzhydrazide	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	p-Dimethyoxybenzene	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Phenylacetone Ketomine	0.84	0.04	0.00	0.11	0.00	0.00	0.00
	Phenethyl-2-methylbutyrate	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	1-Methyl-1,4-Cyclohexadiene	0.57	0.00	0.00	0.00	0.00	0.00	0.00
	2-Methoxylpyridine	0.00	0.94	0.00	0.00	0.00	0.00	0.00
	p-Cresol	0.00	0.03	0.00	0.00	0.00	0.00	0.16
	Methyl Acetyl Dithiocarbomate	0.00	0.00	0.00	0.00	0.00	0.00	2.01

APPENDIX C

COMPILATION DATA FROM EXPERIMENTS

Table C-1: Experimental data on biomass gasification index (BGI), tar content, emissions of CO, NO, SO_2 in different operating parameters, palm shells particle size, and percentage of HZSM-5 catalyst used.

No.	Nitrogen Flowrate (LPM)	Air Flowrate (LPM)	Palm Shells Size (mm)	HZSM-5 Catalyst (Weight %)	BGI (%)	Tar Content (mg/Nm^3)	CO (ppm)	NO (ppm)	SO_2 (ppm)
1	3	5	1.18	0	78.0	158	10667.0	247.0	8.0
2	3	5	1.18	0	80.0	163	10782.0	235.0	6.0
3	3	5	1.18	0	84.0	141	10721.0	271.0	11.0
4	5	5	3.56	0	83.0	1440	9488.0	243.0	301.0
5	5	5	3.56	0	79.0	1510	9328.0	256.0	340.0
6	5	5	3.56	0	86.0	1468	9278.0	238.0	290.0
7	7	5	1.18	0	78.0	1206	11500.0	96.0	0.0
8	7	5	7.13	0	89.0	3122	11103.0	1146.0	0.0
9	7	5	1.18	0	81.0	1234	11238.0	108.0	2.0
10	7	5	7.13	0	85.0	3018	11215.0	1132.0	1.0
11	7	5	7.13	0	92.0	3089	11009.0	1131.0	3.0
12	3	5	1.18	2	76.0	3000	9.0	5.7	1.0
13	3	5	1.18	2		3289			
14	3	5	1.18	2		2874			
15	3	5	3.56	2	81.0	6833	17.6	4.3	0.4
16	3	5	3.56	2		7594			
17	3	5	3.56	2		6598			
18	3	5	7.13	2	80.9	7835	0.0	2.6	1.0
19	3	5	7.13	2		8023			
20	3	5	7.13	2		7698			
21	3	5	1.18	5	73.0	1104	2.8	2.0	1.0
22	3	5	1.18	5		1500			
23	3	5	1.18	5		865			
24	3	5	3.56	5	81.8	1040	17.9	2.2	0.8
25	3	5	3.56	5		1236			
26	3	5	3.56	5		986			
27	3	5	7.13	5	84.0	6667	14.0	5.1	1.0
28	3	5	7.13	5		6487			
29	3	5	7.13	5		6798			
30	3	5	1.18	10	72.9	438	24.3	4.1	0.0
31	3	5	1.18	10		520			

32	3	5	1.18	10		398			
33	3	5	3.56	10	79.2	524	19.1	4.6	0
34	3	5	3.56	10		488			
35	3	5	3.56	10		587			
36	3	5	7.13	10	79.2	561	15.7	0.0	1.4
37	3	5	7.13	10		548			
38	3	5	7.13	10		579			
39	5	5	1.18	2	70.8	2033	8.0	5.5	1.0
40	5	5	1.18	2		2198			
41	5	5	1.18	2		1998			
42	5	5	3.56	2	81.0	4600	5.1	6.2	0.8
43	5	5	3.56	2		4872			
44	5	5	3.56	2		4574			
45	5	5	7.13	2	84.3	5638	6.6	2.9	0.1
46	5	5	7.13	2		5547			
47	5	5	7.13	2		5403			
48	5	5	1.18	5	73.8	333	9.8	3.2	1.0
49	5	5	1.18	5		357			
50	5	5	1.18	5		328			
51	5	5	3.56	5	80.9	717	16.0	5.0	0.7
52	5	5	3.56	5		732			
53	5	5	3.56	5		726			
54	5	5	7.13	5	85.6	873	14.0	2.2	1.0
55	5	5	7.13	5		864			
56	5	5	7.13	5		924			
57	5	5	1.18	10	66.9	50	10.0	4.7	1.0
58	5	5	1.18	10		68			
59	5	5	1.18	10		72			
60	5	5	3.56	10	78.2	86	17.0	3.6	1.0
61	5	5	3.56	10		93			
62	5	5	3.56	10		73			
63	5	5	7.13	10	77.7	92	20.0	0.0	1.0
64	5	5	7.13	10		135			
65	5	5	7.13	10		107			
66	7	5	1.18	2	76.7	2903	19.0	19.0	0.2
67	7	5	1.18	2		3102			
68	7	5	1.18	2		2874			
69	7	5	1.18	5	73.1	1778	8.2	5.7	0.7
70	7	5	1.18	5		1873			
71	7	5	1.18	5		1687			
72	7	5	1.18	10	72.1	861	2.3	4.3	1.0
73	7	5	1.18	10		842			
74	7	5	1.18	10		874			

75	7	5	3.56	2	72.1	3195	12.0	12.0	1.0
76	7	5	3.56	2		3210			
77	7	5	3.56	2		3014			
78	7	5	3.56	5	79.9	2083	5.7	3.2	1.0
79	7	5	3.56	5		2141			
80	7	5	3.56	5		1874			
81	7	5	3.56	10	76.7	1431	1.0	1.0	1.0
82	7	5	3.56	10		1487			
83	7	5	3.56	10		1520			
84	7	5	7.13	2	83.2	4722	9.4	9.4	1.0
85	7	5	7.13	2		4802			
86	7	5	7.13	2		4630			
87	7	5	7.13	5	81.3	3694	3.2	14.0	1.0
88	7	5	7.13	5		3520			
89	7	5	7.13	5		3720			
90	7	5	7.13	10	78.0	2986	17.0	28.0	1.0
91	7	5	7.13	10		2874			
92	7	5	7.13	10		2784			